



PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE HONORABLE BOARD OF PATENT APPEALS AND INTERFERENCES

In re the Application of

Toru NOGUCHI et al.

Application No.: 10/821,175

Examiner: E. COLE

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Docket No.: 127794

For: CARBON FIBER COMPOSITE MATERIAL AND PROCESS FOR PRODUCING THE  
SAME

BRIEF ON APPEAL

Appeal from Group 1794

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**I. REAL PARTY IN INTEREST**

The real party in interest for this appeal and the present application is Nissin Kogyo Co., Ltd., by way of an Assignment recorded in the U.S. Patent and Trademark Office at Reel 015597, Frame 0431.



**II. RELATED APPEALS AND INTERFERENCES**

There are no prior or pending appeals, interferences or judicial proceedings, known to Appellants, Appellants' representative, or the Assignee, that may be related to, or that will directly affect or be directly affected by or have a bearing upon, the Board's decision in the pending appeal.

**III. STATUS OF CLAIMS**

Claims 1-3, 6-10, 23, 24 and 26-29 are on appeal.

Claims 1-3, 6-24 and 26-29 are pending.

Claims 1-3, 6-10 23, 24 and 26-29 are rejected.

Claims 11-22 are withdrawn from consideration.

Claims 4, 5 and 25 are canceled.

**IV. STATUS OF AMENDMENTS**

No Amendment After Final Rejection has been filed.

**V. SUMMARY OF CLAIMED SUBJECT MATTER**

The summary of the subject matter of independent claims 1, 7, 8, 27 and 28 is given below with reference to the specification, as published in U.S. Patent Publication No. 2004/0241440. Appellants note that the specification has been amended since publication, and rely upon the amended text of the specification. Any reference to the specification is only exemplary and should neither be construed to encompass every portion of the specification that supports the claim features nor construed to limit the claimed subject matter beyond the claim language.

Claim 1 is directed to a carbon fiber composite material. *See* paragraph [0061]. The carbon fiber composite material has a plurality of carbon nanofibers 40 that are substantially uniformly dispersed in an elastomer 30. *See* Fig. 1 and paragraphs [0034]-[0050]. The elastomer has either an unsaturated bond or a group that has an affinity to the carbon nanofibers. *See* paragraph [0039]. The elastomer is also in its uncrosslinked form. *See* paragraph [0064]. The composite material has a first spin-spin relaxation time ( $T_{2n}$ ) of 100 to 3,000  $\mu\text{sec}$ . *See* paragraph [0064]. The composite material also has a second spin-spin relaxation time ( $T_{2nn}$ ) of being absent or 1,000 to 10,000  $\mu\text{sec}$ . *See* paragraph [0064]. A fraction ( $f_{nn}$ ) of components having the second spin-spin relaxation time, as compared to components having the first spin-spin relaxation time, is less than 0.2. *See* paragraphs [0064] and [0086]. The spin-spin relaxation times are measured under conditions of an observing nucleus of  $^1\text{H}$  at 150 °C by the Hahn-echo method using pulsed NMR technique. *See* paragraph [0086].

Claim 7 is directed to a carbon fiber composite material. *See* paragraph [0061]. The carbon fiber composite material has a plurality of carbon nanofibers 40 that are substantially uniformly dispersed in an elastomer 30. *See* Fig. 1 and paragraphs [0034]-[0050]. The elastomer is in its uncrosslinked form. *See* paragraph [0064]. The composite material has a

first spin-spin relaxation time ( $T_{2n}$ ) of 100 to 3,000  $\mu\text{sec}$ . *See* paragraph [0064]. The composite material also has a second spin-spin relaxation time ( $T_{2nn}$ ) of being absent or 1,000 to 10,000  $\mu\text{sec}$ . *See* paragraph [0064]. A fraction ( $f_{nn}$ ) of components having the second spin-spin relaxation time, as compared to components having the first spin-spin relaxation time, is less than 0.2. *See* paragraphs [0064] and [0086]. The spin-spin relaxation times are measured under conditions of an observing nucleus of  $^1\text{H}$  at 150 °C by the Hahn-echo method using pulsed NMR technique. *See* paragraph [0086].

Claim 8 is directed to a carbon fiber composite material. *See* paragraph [0061]. The carbon fiber composite material has a plurality of carbon nanofibers 40 that are substantially uniformly dispersed in an elastomer 30. *See* Fig. 1 and paragraphs [0034]-[0050]. The elastomer is in its crosslinked form. *See* paragraph [0065]. The composite material has a first spin-spin relaxation time ( $T_{2n}$ ) of 100 to 2,000  $\mu\text{sec}$ . *See* paragraph [0065]. The composite material also has a second spin-spin relaxation time ( $T_{2nn}$ ) of being absent or 1,000 to 5,000  $\mu\text{sec}$ . *See* paragraph [0065]. A fraction ( $f_{nn}$ ) of components having the second spin-spin relaxation time, as compared to components having the first spin-spin relaxation time, is less than 0.2. *See* paragraphs [0065] and [0086]. The spin-spin relaxation times are measured under conditions of an observing nucleus of  $^1\text{H}$  at 150 °C by the Hahn-echo method using pulsed NMR technique. *See* paragraph [0086].

Claim 27 is directed to a carbon fiber composite material. *See* paragraph [0061]. The carbon fiber composite material has a plurality of carbon nanofibers 40 that are substantially uniformly dispersed in an elastomer 30. *See* Fig. 1 and paragraphs [0034]-[0050]. The elastomer has either an unsaturated bond or a group that has an affinity to the carbon nanofibers. *See* paragraph [0039]. The elastomer is also in its crosslinked form. *See* paragraph [0065]. The composite material has a first spin-spin relaxation time ( $T_{2n}$ ) of 100 to 2,000  $\mu\text{sec}$ . *See* paragraph [0065]. The composite material also has a second spin-spin

relaxation time ( $T_{2n}$ ) of being absent or 1,000 to 5,000  $\mu\text{sec}$ . *See* paragraph [0065]. A fraction ( $f_{nn}$ ) of components having the second spin-spin relaxation time, as compared to components having the first spin-spin relaxation time, is less than 0.2. *See* paragraphs [0065] and [0086]. The spin-spin relaxation times are measured under conditions of an observing nucleus of  $^1\text{H}$  at 150 °C by the Hahn-echo method using pulsed NMR technique. *See* paragraph [0086].

Claim 28 is directed to a carbon fiber composite material. *See* paragraph [0061]. The carbon fiber composite material has a plurality of carbon nanofibers 40 that are homogenously dispersed in an elastomer 30. *See* Fig. 1 and paragraphs [0034]-[0050]. The elastomer has either an unsaturated bond or a group that has an affinity to the carbon nanofibers. *See* paragraph [0039].

**VI. GROUND OF REJECTION TO BE REVIEWED ON APPEAL**

The following grounds of rejection are presented for review:

- 1) Claims 1-3, 6-10, 23, 24 and 26-29 are rejected under 35 U.S.C. §103(a) over WO 03/060002 to Kim in view of U.S. Patent No. 5,844,523 to Brennan et al. ("Brennan").
- 2) Claims 1-3, 6-10, 23, 24 and 26-29 are rejected under 35 U.S.C. §103(a) over U.S. Patent No. 6,203,814 to Fisher et al. ("Fisher") in view Brennan.

## VII. ARGUMENT

Appellants respectfully request this Board to reverse the two rejections of claims 1-3, 6-10, 23, 24 and 26-29. First, none of the applied references discloses that "the composite material has a first spin-spin relaxation time ( $T_{2n}$ ) of 100 to 3,000  $\mu\text{sec}$  and a second spin-spin relaxation time ( $T_{2nn}$ ) of being absent or 1,000 to 10,000  $\mu\text{sec}$ " and the Final Rejection's assertion that this feature is inherent to the references lacks merit. Second, none of the applied references discloses or renders obvious a composite material having carbon nanofibers substantially uniformly dispersed in the elastomer. Finally, the evidence presented during prosecution demonstrates that the claimed invention fulfilled a long felt, but unmet need in the art. For all these reasons the rejections should be reversed.

### A. Independent Claims 1, 7, 8 and 27 Would Not Have Been Obvious Over Kim in View of Brennan

The combinations of features recited in independent claims 1, 7, 8 and 27 are not disclosed or suggested by Kim and Brennan for at least two reasons. First, Kim does not inherently disclose the recited spin-spin relaxation times. Second, Kim does not disclose that the plurality of carbon nanofibers are substantially uniformly dispersed in the elastomer.

#### 1. Kim Does Not Inherently Disclose the Recited Spin-Spin Relaxation Times

Independent claim 1 recites that "the composite material has a first spin-spin relaxation time ( $T_{2n}$ ) of 100 to 3,000  $\mu\text{sec}$  and a second spin-spin relaxation time ( $T_{2nn}$ ) of being absent or 1,000 to 10,000  $\mu\text{sec}$ ." Claim 1 further recites that the fraction ( $f_{nn}$ ) of components that have the second spin-spin relaxation time is less than 0.2. Independent claims 7, 8 and 27 recite similar features.

The August 14, 2009 Final Rejection ("the Final Rejection") concedes that Kim and Brennan do not explicitly disclose these spin-spin relaxation times. *See* Final Rejection,



section 2, page 2. Rather, the Final Rejection asserts that this feature is inherent to the applied references. *See* Final Rejection, section 2, page 2.

Specifically, the Final Rejection asserts that because Kim discloses that "the same materials are employed and the same results are obtained, it is reasonable to presume that the materials of [Kim] would have the claimed spin-spin relaxation time." *See* Final Rejection, section 2, page 2. As discussed at length below, Appellants dispute that the same results are obtained. But even if the same results are obtained, the recited spin-spin relaxation times are not inherent features of the final product that would be produced by the process of Kim.

To establish inherency, the extrinsic evidence must make clear that the missing descriptive matter is necessarily present and that it would be so recognized by a person of ordinary skill. *In re Robertson*, 169 F.3d 743 (Fed. Cir. 1999). Inherency may not be established by probabilities or possibilities. *Id.* The mere fact that a certain thing may result from a given set of circumstances is not sufficient to support an inherency rejection. *Id.* In this case, spin-spin relaxation time can depend on several factors that vary in the applied references.

Kim allegedly reinforces rubber by adding carbon nanotubes and dispersing them into the rubber. The Final Rejection asserts that the same raw materials are used (i.e., rubber and nanotubes), and a material with the same desired effect is produced (reinforced rubber). *See* Final Rejection, section 2, page 2. As such, the Final Rejection asserts that the final product must have the recited spin-spin relaxation times.

The rejection lacks merit because the Final Rejection ignores that fabrication of a material can alter the properties of the material, even if identical raw materials are used as a starting point of the fabrication processes. Consider by analogy the fabrication of steel. Many steels with different properties are fabricated using identical raw materials merely by altering the fabrication process. For example, if two identical pieces of raw steel are cooled

differently, one by quenching the other by air cooling, the two final pieces of steel will have different properties.

Similarly reinforced rubber can have different properties based on how it is fabricated. This is demonstrated by the May 7, 2009 Declaration of Mr. Toru Noguchi (submitted with the May 11, 2009 Amendment). Mr. Noguchi conducted a series of tests. The purpose of the tests was to examine the effect that the method of mixing the components had on the final composite product. In these tests the same raw materials were used. *See* May 7, 2009 Declaration of Mr. Toru Noguchi, item 9. Specifically, in the experiments EPDM 100 parts by weight (phr) was used as the primary elastomer. *See* May 7, 2009 Declaration of Mr. Toru Noguchi, item 9. Carbon nanofibers with an average diameter of 13nm in the amount of 10 phr and peroxide (DCP) 2 phr were used as crosslinking agents. *See* May 7, 2009 Declaration of Mr. Toru Noguchi, item 9.

Each identical set of materials was mixed using one of three different mixing methods (methods A-C). *See* May 7, 2009 Declaration of Mr. Toru Noguchi, item 10. Mixing method A was a shear rolling method as described in Apellants' specification. *See* May 7, 2009 Declaration of Mr. Toru Noguchi, item 12. Mixing method B was a general mixing method using a Labo Plastmill (Banbury mixer style). *See* May 7, 2009 Declaration of Mr. Toru Noguchi, item 13. Mixing method C used a twin screw extruder, shown in attached Fig. 3. *See* May 7, 2009 Declaration of Mr. Toru Noguchi, item 15.

The results of the tests show that Method A resulted in a first spin-spin relaxation time of 1860  $\mu$ s and a second spin-spin relaxation time of 6100  $\mu$ s. *See* May 7, 2009 Declaration of Mr. Toru Noguchi, Table 1. These values lie in the ranges defined in claim 1. By contrast, Method B resulted in a first spin-spin relaxation time of 3200  $\mu$ s and a second spin-spin relaxation time of 12000  $\mu$ s. *See* May 7, 2009 Declaration of Mr. Toru Noguchi, Table 1. Method C resulted in a first spin-spin relaxation time of 3900  $\mu$ s and a second spin-spin

relaxation time of 17000  $\mu$ s. *See* May 7, 2009 Declaration of Mr. Toru Noguchi, Table 1. These spin-spin relaxation times lie outside the recited range.

Thus, the spin-spin relaxation times vary based on mixing method. In other words, specific spin-spin relaxation times are not an inherent property of raw material and final product, as alleged by the Final Rejection. Rather, spin-spin relaxation times vary based on fabrication methods such as mixing methods.

This demonstrates that the recited spin-spin relaxation times would not necessarily be present in the reinforced rubber disclosed by Kim. As noted earlier, a feature is only inherent if it is necessarily present in a reference. *In re Robertson*, 169 F.3d at 745.

Appellants also note that the text of the Final Rejection itself demonstrates the deficiency of the rejection. The Final Rejection states that "since the same materials are employed and the same results obtains, it is reasonable to presume that the materials of [Kim] would have the claimed spin-spin relaxation time." *See* Final Rejection, section 2, page 2 (emphasis added). But case law states that inherency may not be established by probabilities or possibilities. *In re Robertson*, 169 F.3d at 745. The rejection must establish that the feature will necessarily be present. The conclusion drawn in the Final Rejection does not even meet this threshold. Thus, the rejection is deficient on its face.

For at least the above reasons, Kim does not inherently disclose the recited spin-spin relaxation times.

**a. The Final Rejection's Rebuttals to the Arguments of the May 11 Amendment**

The August 14, 2009 Final Rejection presents three rebuttals to the above arguments. First, the Final Rejection asserts that Appellants' specification does not disclose that a specific type of mixing is required. Second, the Final Rejection asserts that the claims do not recite that any specific method of mixing is required. Third, the Final Rejection asserts that because

Kim discloses uniform dispersion it necessarily discloses the recited spin-spin relaxation times because they are related. Appellants summarize and respond to each rebuttal below.

**b. It is Irrelevant That the Specification Discloses Multiple Mixing Methods**

The Final Rejection asserts that Appellants' specification indicates that multiple methods of mixing can be used to produce the recited product. *See* Final Rejection page 5, item 6. The Final Rejection quotes Appellants' specification, which states "it is only required in this [mixing] step to apply shear force sufficient to separate the aggregated fibrils." *See* Final Rejection, section 6, pages 5-6, citing Appellants' specification, paragraph [0057]. Thus, the Final Rejection appears to conclude that the May 7, 2009 Declaration of Mr. Toru Noguchi can be ignored because it contradicts the specification.

This alleged contradiction is irrelevant to whether Kim inherently discloses the recited spin-spin relaxation times for two reasons. First, there is no contradiction between the Declaration and the specification. Different mixing methods can be used to make Appellants' material if fabrication and raw material choice is tailored for the particular mixing method. (See the discussion of paragraphs [0054], [0056] and [0057] set forth below.) Second, the May 7, 2009 Declaration of Mr. Toru Noguchi was provided to show that spin-spin relaxation times can vary according to at least one fabrication step. As such, the Declaration establishes that other manufacturing methods will affect the spin-spin relaxation times.

The Final Rejection implies that the results of the May 7, 2009 Declaration of Mr. Toru Noguchi should be ignored merely because Appellants' specification implies that all of the mixing methods disclosed in his Declaration can be used to fabricate the claimed material. This is an improper interpretation of Appellants' specification. Appellants' specification requires that several factors be tailored, depending on the mixing method choice, in order to fabricate the claimed material.

For example, paragraph [0057] (cited by the Final Rejection) states that other mixing methods can be used if they apply sufficient shear force to separate aggregated carbon nanofibers. But paragraph [0056] explains that the proper level of shear force is affected and dependent on the chosen elastomer. Specifically, paragraph [0056] of Appellants' specification explains that when a "high shear force is applied" to an elastomer, "having an appropriate molecular length and a high molecular mobility" then the aggregated carbon nanotubes will be dispersed. But if the choice of elastomer is not tailored to the type of mixing method, the material may not have the recited spin-spin relaxation times. Also if the mixing method fails to provide sufficient shear force the resulting material may not have the recited spin-spin relaxation times.

Furthermore, paragraph [0054] explains that mixing temperature may vary depending on the mixing method chosen. Thus, if the mixing temperature is not tailored to the type of mixing method the final product may not have the recited spin-spin relaxation times.

None of these factors alters the fact that the May 11, 2009 Declaration of Mr. Toru Noguchi conclusively demonstrates that if a different mixing method is used without such tailoring, the final results will have varying spin-spin relaxation times. The applied references fail to disclose how to tailor fabrication to obtain the recited spin-spin relaxation times. Thus, if different mixing methods were used on the raw materials of Kim, the resulting products would have different spin-spin relaxation times.

Furthermore, the May 7, 2009 Declaration of Mr. Toru Noguchi was only used to demonstrate that altering at least one fabrication step could alter the spin-spin relaxation times. Other changes in fabrication may also affect the spin-spin relaxation times. Prior to the May 11, 2009 Declaration of Mr. Toru Noguchi, the Examiner asserted that the Examiner she had established a *prima facie* case of inherency. By demonstrating that the mixing method affects spin-spin relaxation time, Appellants have effectively rebutted the Examiner's



inherency assertion. The Examiner is not longer entitled to any presumption that other steps of manufacture (beyond mixing methods) will not also affect spin-spin relaxation time. The Final Rejection fails to present any evidence regarding its inherency allegations. Thus, the Final Rejection fails to present a *prima facie* case of inherency.

c. **It is Irrelevant That the Claims Do Not Recite a Specific Mixing Method**

The Final Rejection also asserts that the May 7, 2009 Declaration of Mr. Toru Noguchi fails to overcome the rejection because claims 1, 7, 8 and 27 fail to recite a specific mixing method. This rebuttal also lacks merit.

As discussed above, to establish inherency, the extrinsic evidence must make clear that the missing descriptive matter is necessarily present. *In re Robertson*, 169 F.3d at 745. The claims recite two specific spin-spin relaxation times. It is the Examiner's burden to demonstrate that Kim will always produce a final product having these spin-spin relaxation times when the same raw materials are used.

Mr. Noguchi's May 7, 2009 Declaration establishes that different mixing methods will affect the spin-spin relaxation times and therefore many of the resulting products will not have the claimed relaxation times. Thus, the Declaration establishes that Kim does not inherently produce a composite material having the recited spin-spin relaxation times.

As described previously, Appellants' disclosure teaches that different mixing methods can be used as long as various parameters are controlled so as to achieve the claimed relaxation times. Thus, it is not necessary for Appellants' claims to recite a particular mixing method. As such, the Final Rejection's rebuttal lacks merit.

d. **Kim Fails to Disclose the Relationship Between Spin-Spin Relaxation Time and Dispersion**

The Final Rejection's last rebuttal is that Appellants' July 31, 2006 Response states that spin-spin relaxation time is an indicator that a material has uniform dispersion of

nanofibers. See Final Rejection, Section 6, page 6. The Final Rejection argues that Kim discloses a material with substantially uniform dispersion of nanofibers. Thus, the Final Rejection reasons that this material must inherently have the recited spin-spin relaxation times.

As a preliminary matter, Appellants again first dispute that Kim discloses a material with substantially uniform dispersion of nanofibers. But assuming *arguendo* that Kim discloses uniformly dispersed nanofibers, the prior art does not disclose that such a material inherently has the recited spin-spin relaxation times. Rather, the relationship between dispersion and spin-spin relaxation time is only disclosed in Appellants' specification. The inherency of a feature cannot be proven using hindsight based on a relationship discovered and disclosed in an applicant's specification. *In re Rejckaert*, 9 F.3d 1531, 1533 (Fed. Cir. 1993); *also see* MPEP §2142.02(V) stating "obviousness cannot be predicated on what is not known at the time an invention is made, even if the inherency of a certain feature is later established." Instead, the prior art itself must prove the relationship.

The applied references do not disclose a relationship between nanofiber dispersion and spin-spin relaxation time. In fact the applied references do not even disclose the existence of spin-spin relaxation times. Thus, the prior art fails to show that a material having uniform dispersion will also have the recited spin-spin relaxation times. Any suggestion otherwise is the product of hindsight. Thus, the Final Rejection's rebuttal lacks merit.

2. **Kim Does Not Disclose or Render Obvious Substantially Uniform Dispersion**

Claim 1 recites "a plurality of carbon nanofibers substantially uniformly dispersed in the elastomer." The Final Rejection asserts that Kim discloses substantially uniform dispersion of carbon nanotubes in natural rubber. See Final Rejection, section 2, page 2. But

Kim only discloses a method for more uniform dispersion of the carbon nanotubes, as compared to previous methods. See Kim, page 5. Kim does not disclose substantially uniform dispersion. Furthermore, the Bokobza article establishes that known methods (such as Kim) had not resulted in substantially uniform dispersion as of the filing date of this application.

a. **Substantially Uniform Dispersion Requires Homogenous Distribution of the Nanofibers Through the Elastomer**

Substantially uniform dispersion requires that the nanofibers be homogeneously dispersed in the elastomer, with the word "substantially" accounting for the normal non-perfection that is inherent in any human endeavor. Appellants' specification explains that nanofibers have a strong tendency to aggregate into clumps. See Appellants' specification, paragraph [0002]. The specification explains that this aggregation inhibits a homogenous dispersion of the nanofibers. See Appellants' specification, paragraph [0002]. The specification explains that the material produced by Appellants' method has homogeneously dispersed the nanofibers into the elastomer, and prevents them from reaggregating. Appellants' specification, paragraph [0061].

b. **Kim Only Discloses Obtaining More Uniform Dispersion Than Was Previously Possible**

The Final Rejection asserts that Kim discloses the recited feature of substantially uniform distribution. But Kim only discloses improving nanofiber distribution (over the previous art). See Kim, page 5. In other words, Kim only discloses that it moved closer to the goal of substantially uniform dispersion than those before. Kim does not disclose that it reached this goal.

As evidence, consider the text of Kim. Page 5, line 13 of Kim refers to an "improvement for more uniformly distributing carbon nanotubes." (emphasis added). Likewise, line 19 refers to more uniform distribution and lines 21-22 state that the surfactants



"helped to improve uniform distribution." (emphasis added). The text of Kim shows that it only discloses an improvement in distribution, as compared to earlier materials. But Kim implies that further improvements are still needed to achieve homogenous distribution.

The only statement in Kim that does not contain a qualifier is found in lines 27-28, which state "the surfactants...are not limited in type as long as they distribute carbon nanotubes or GNF uniformly in the rubber." But Kim provides no disclosure or enablement of such uniform dispersion. Appellants respectfully submit that the totality of Kim shows the Mr. Kim believed he was in possession of an improvement, but Mr. Kim did not believe he had achieved substantially uniform dispersion.

c. **The Bokobza Article Rebuts The Final Rejection's Assertion That Kim Had Achieved Substantially Uniform Distribution**

As further evidence that Kim does not disclose or suggest substantially uniform dispersion of nanofibers, Appellants point to Liliane Bokobza's 2007 article entitled Multiwall carbon nanotube elastomeric composites: A review (submitted in the May 11, 2009 IDS) (hereinafter "Bokobza"). This article was published several years after Kim. Bokobza explains that it is difficult "to obtain a homogeneous dispersion of carbon nanotubes in a polymer matrix because van der Waals interactions between individual tubes lead to significant aggregation or agglomeration." *See* Bokobza, page 4908, col. 2.

Bokobza also explains that numerous attempts to optimize dispersion have been made. Bokobza specifically identifies that "chemical functionalization" was one of the attempted methods. *See* Bokobza, page 4908, col. 2. This is the same method allegedly disclosed by Fisher, as will be discussed further below. Yet Bokobza states that in 2007 poor dispersion continued to "limit the full utilization of carbon nanotubes for reinforcing polymeric media." *See* Bokobza Abstract. In other words, Bokobza discloses that several

years after Kim, no method had achieved substantially uniform dispersion of nanotubes in an elastomer, such as natural rubber.

As such, Appellants respectfully submit that Bokobza conclusively rebuts any assertion that Kim either discloses substantially uniform distribution or that one of ordinary skill could have optimized Kim to achieve substantially uniform distribution. Rather, Liliane Bokobza, a person of ordinary skill in the art at the time of Appellants' invention, did not believe that substantially uniform dispersion of carbon nanofibers had been achieved.

**B. Independent Claims 1, 7, 8 and 27 Would Not Have Been Obvious Over Fisher in View of Brennan**

The combination of features of independent claims 1, 7, 8 and 27 are also not disclosed or rendered obvious by the combination of Fisher and Brennan. First, Fisher does not inherently disclose the recited spin-spin relaxation times. Second, Fisher does not disclose a material with substantially uniformly dispersed nanofibers. Because many of the arguments in this section mirror those presented above, this section will emphasize aspects of the previous arguments in light of Fisher.

**1. Fisher Does Not Inherently Disclose the Recited Spin-Spin Relaxation Times**

As discussed earlier, claim 1 recites that "the composite material has a first spin-spin relaxation time ( $T_{2n}$ ) of 100 to 3,000  $\mu\text{sec}$  and a second spin-spin relaxation time ( $T_{2nn}$ ) of being absent or 1,000 to 10,000  $\mu\text{sec}$ ...[and] a fraction ( $f_{nn}$ ) of components having the second spin-spin relaxation time of less than 0.2." Claims 7, 8 and 27 recite similar features.

The Final Rejection concedes that Fisher and Brennan do not explicitly disclose these spin-spin relaxation times. *See* Final Rejection, section 3, page 4. Rather, the Final Rejection asserts that this feature is inherent because Fisher uses the same raw materials and obtains the same product as Appellants. *See* Final Rejection, section 3, page 4. For the same reasons

articulated above, the recited spin-spin relaxation times are not an inherent feature of the final product produced by Fisher and Brennan.

To establish inherency, the extrinsic evidence must make clear that the missing descriptive matter is necessarily present and that it would be so recognized by person of ordinary skill. *In re Robertson*, 169 F.3d 743 (Fed. Cir. 1999). The mere fact that a certain thing may result from a given set of circumstances is not sufficient to support an inherency rejection. As explained above, spin-spin relaxation time can depend on several factors that vary in the applied references.

Appellants again note that the May 7, 2009 Declaration of Mr. Toru Noguchi demonstrates that even if the same raw materials are used to produce the same final product, the recited spin-spin relaxation times vary considerably. The May 7, 2009 Declaration of Mr. Toru Noguchi also demonstrates that this variation results in spin-spin relaxation times outside the recited range. This rebuts the assertions made in section 3 of the Final Rejection.

Appellants also stand on their earlier counter-arguments to the rebuttals of the Final Rejection relating to this argument.

**2. Fisher Does Not Disclose or Render Obvious Substantially Uniform Dispersion**

Claims 1, 7, 8 and 27 substantively recite a material in which a plurality of carbon nanofibers are uniformly dispersed in an elastomer. The Final Rejection asserts that Fisher renders this feature obvious. *See* Final Rejection, section 3, page 4. Specifically, the Final Rejection explains that Fisher discloses functionalizing carbon fibrils. *See* Final Rejection, section 3, page 4. This process involves bonding functional groups to the surfaces of the fibrils. *See* Final Rejection, section 3, page 4. Fisher allegedly discloses that the functional groups allows the fibrils (the alleged nanofibers) to disperse better into a polymer system (the alleged elastomer). *See* Final Rejection, section 3, page 4. The Final Rejection concludes

that "it would have been obvious to have selected the functional groups which produced the best dispersion of the functionalized fibrils into the polymer system." *See* Final Rejection, section 3, page 4.

However, this assertion is contradicted by Bokobza. As noted above, Bokobza discusses the state of the art as it existed in 2007. Bokobza explains that it is difficult "to obtain a homogeneous dispersion of carbon nanotubes in a polymer matrix because van der Waals interactions between individual tubes lead to significant aggregation or agglomeration." *See* Bokobza, page 4908, col. 2.

Bokobza also specifically identifies "chemical functionalization" as one of the numerous attempts that had been tried in the field to optimize dispersion. *See* Bokobza, page 4908, col. 2. This is the same method disclosed by Fisher. Bokobza states that the chemical functionalization approach was successful in epoxy matrices. *See* Bokobza, page 4909, col. 1. Yet Bokobza states that poor dispersion continues to "limit the full utilization of carbon nanotubes for reinforcing polymeric media." *See* Bokobza Abstract (emphasis added). Fisher discloses using chemical functionalization to disperse nanotubes in polymers. *See* Fisher, col. 7, lines 1-18. Yet Bokobza discloses that chemical functionalization had not yet yielded substantially uniform dispersion in polymers as of 2007.

Bokobza's statements conclusively rebut the Final Rejection's assertion that one of ordinary skill in the art could have modified and perfected the system of Fisher to achieve substantial uniform dispersion. To the contrary, the Bokobza article shows that Fisher cannot produce the recited feature.

a. **The Final Rejection's Rebuttal to the Above Arguments and Appellant's Counter-Argument**

The Final Rejection attempts to rebut the above arguments by asserting that "Bokobza does not dismiss functionalization as failed but instead states that

functionalization...can be used to improve dispersion." See Final Rejection, section 8, page 8. The Final Rejection appears to assert that improving dispersion discloses the features of claims 1, 7, 8, and 27. This assertion lacks merit.

The Final Rejection is correct that Bokobza indicates that functionalization can improve dispersion. But claims 1, 7, 8 and 27 do not recite a material merely having improved dispersion. Rather, the claims recite substantially uniform dispersion. Fisher disclosed a method for moving closer to a goal that only Appellants reached. Bokobza shows that Fisher fails to reach homogenous dispersion. To put it another way, the Final Rejection states that it would have been obvious to select the functional group that "produced the best dispersion." See Final Rejection, section 3, page 4. But Fisher's "best" was just not good enough.

Thus, for at least the reasons above, the combination of Fisher and Brennan does not disclose or render obvious the features of independent claims 1, 7, 8 and 27.

**C. Independent Claim 28 Would Not Have Been Obvious Over Kim and Brennan or Fisher and Brennan**

Independent claim 28 recites a carbon fiber composite material comprising an elastomer and a plurality of carbon nanofibers homogeneously dispersed in the elastomer. As discussed earlier, the claim term "substantially uniformly dispersed" is synonymous with the term homogeneously dispersed.

Appellants respectfully submit that the applied references do not disclose a carbon fiber material having the carbon nanofibers homogeneously dispersed in the elastomer for the same reasons (presented above) that the references do not disclose substantially uniform dispersion. Thus, the applied references fail to disclose or render obvious the features of claim 28.

**D. The Claimed Invention Fulfilled a Long Felt, But Unmet Need in the Art**

MPEP §2144.05(III) states that a *prima facie* case of obviousness can be rebutted if the Applicant can demonstrate that the invention fulfilled a long felt, but unmet need in an art. Establishing a long-felt need requires objective evidence that (1) an art recognized problem (2) existed in the art for a long period of time (3) without solution. MPEP §716.04. The MPEP also clarifies that (4) the claimed invention must "satisfy the long felt need." MPEP §716.04. The evidence in the record establishes all four of these elements.

1. **Those of Ordinary Skill in the Art Had Been Trying to Achieve Uniform Dispersion for at Least Nine Years Prior to the Filing Date of this Application**

The evidence in the record indicates that those of ordinary skill in the art (1) recognized that uniform dispersion of nanofibers in an elastomer would be of great value and (2) were working to achieve this goal from at least 1994 to 2003. This evidence includes the August 20, 2008 Declaration of Mr. Toru Noguchi (submitted with the August 25, 2008 Amendment), the prior art cited by the Examiner, and additional references submitted by Appellants.

First, in his August 20, 2008 Declaration, Mr. Toru Noguchi certified that "it was known in the field of carbon fiber composite materials that substantially uniform dispersion of carbon nanofibers in a carbon fiber composite material would create a composite material having advantageous properties." See August 20, 2008 Declaration of Mr. Toru Noguchi. Mr. Noguchi has both extensive education, experience and credentials in the field. Thus, his sworn assertions must be given weight.

Second, both Fisher and Kim desired to improve dispersion of carbon nanofibers. Both references explain that introducing and dispersing carbon nanofibers into an elastomer would improve the tensile strength and properties of the elastomer. See Fisher, col. 7, lines 15-18; Kim, page 5, lines 16-18. Fisher was filed in 1994 and Kim was filed in 2003. Thus, the cited references show that those in the art were working to achieve more uniform



dispersion of carbon nanofibers in rubber and similar elastomers at least between 1994 and 2003.

Finally, as supporting evidence, Appellants attach the 2001 article entitled "Advances in the science and technology of carbon nanotubes and their composites: a review" by Thostenson, et al.<sup>1</sup> Thostenson states that "uniform dispersion within the polymer matrix...are critical issues in the processing of these nanocomposites." *See* Thostenson, section 6.1, page 1907. Thostenson also explains that "nanotube dispersion is critical to efficient reinforcement" but states that it is "difficult to obtain uniform dispersion of carbon nanotubes in the polymer matrix." *See* Thostenson, section 6.1, page 1907. This shows that in 2001 those in the art desired to obtain uniform dispersion of nanotubes in polymers, but were stymied in doing so.

Appellants' priority date is April 9, 2003. Appellants submit that the 1994 to 2003 time frame constitutes a long period of time, as required by the MPEP.

**2. As of April 9, 2004 No One Had Achieved Uniform Dispersion of Carbon Nanofibers in an Elastomer**

The evidence also shows that none of the attempts in the art had been successful prior to 2003. Bokobza states that "dispersing nanotubes into different polymeric matrices have attracted wide attention...one of the biggest challenges is to obtain a homogenous dispersion." *See* Bokobza, page 4908, col. 2, lines 19-28. Yet Bokobza concluded that "despite the fact that much progress has been made in the processing techniques, the mechanical improvement...remains minor." *See* Bokobza, page 4908, col. 2, lines 19-35. Bokobza also states that "poor dispersion and poor interfacial bonding limit the full utilization of carbon nanotubes for reinforcing polymeric media. *See* Bokobza Abstract.

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<sup>1</sup> Thostenson was not previously submitted into the record, but is instead attached to this Appeal Brief as supplementary evidence. Thostenson is a reference cited by the Bokobza article, which is of record.

Mr. Toru Noguchi also stated in his August 20, 2008 Declaration that prior to his, and his co-inventor's work, no one in the art had achieved uniform dispersion. Thus, Appellants submit that the Bokobza article and Mr. Noguchi's statements establish that those of ordinary skill in the art had not achieved substantially uniform dispersion of nanofibers in an elastomer prior to Appellants' disclosure.

**a. The Final Rejection's Rebuttal to the Above Arguments**

The Final Rejection asserts that Appellants failed to demonstrate that "if a person skilled in the art know of the teachings of Fisher and [Kim] that they would still [have been] unable to solve the problem. *See* Final Rejection, section 10, page 9. In other words, the Final Rejection appears to be asserting that Appellants have failed to demonstrate that Bokobza was specifically aware of Fisher and Kim. The Final Rejection further appears to be asserting that because Fisher and Kim allegedly disclose the recited features, and Appellants have failed to specifically show Bokobza was aware of their work, that Appellants have failed to demonstrate those in the art had not solved the long felt need.

**b. Appellant's Counter-Argument to the Final Rejection**

The Final Rejection's rebuttal lacks merit for several reasons. First, the MPEP does not require that an Applicant demonstrate that those in the art were specifically aware of a given reference. Second, as an apparent person of ordinary skill in the art, Ms. Bokobza is presumed to be aware of all art in the field. Third, the Bokobza article makes specific reference to the failure of Fisher's method to achieve homogenous dispersion.

The Final Rejection cites to form paragraph 7.66.04 as evidence that an Appellants must demonstrate that those in the art were aware of the references cited in the Final Rejection. Form paragraph 7.66.04 presents a ground for rejecting a Declaration asserting a long felt, but unmet need. The grounds for rejection state "there is no evidence that if persons skilled in the art who were working on the problem know of the teachings of the above cited



references, they would still be unable to solve the problem." The form paragraph cites to MPEP §716.04 as requiring this evidentiary burden.

But MPEP §716.04 does not place such a burden on an applicant. MPEP §716.04 only states those of ordinary skill must not have previously solved the problem. Appellants submit that §716.04 means that if the prior art discloses a different solution to the long felt need than the claimed solution it would prevent the Applicant from overcoming a rejection under §716.04. But §716.04 makes no reference to a requirement that those of ordinary skill in the art be aware of or specifically supplied with the cited references. The burden of proof required by the Final Rejection does not appear in §716.04.

A stock paragraph that adds a burden of proof upon an applicant that is not required by its corresponding MPEP section should be ignored. The text of the MPEP is controlling over any stock paragraph's interpretation. In Appellants' May 11, 2009 Amendment, Appellants' invited the Examiner to cite to any case law supporting stock paragraph 7.66.04's interpretation of §706.04. The Final Rejection provides no such citations. As such, Appellants respectfully request that this Board find that the Final Rejection has placed a burden of proof upon Appellants that exceeds that authorized by the text of the MPEP.

Furthermore, a person of ordinary skill in the art is presumed to be aware of all relevant art. Both Ms. Bokobza and Mr. Toru Noguchi are representative of persons of ordinary skill in the art. As such, they are entitled to the presumption that they were aware of the cited references.

In fact, the point of showing that an invention has fulfilled a long felt, but unmet need is to remove the hindsight associated with an Examiner's interpretation of a reference from interfering with reality. The theory is premised upon the notion that if real people of skill in the art (rather than a hypothetical person of ordinary skill) have been unable to solve a

problem for a long period of time, this should rebut any hypothetical assumption of what they may have thought was obvious.

Finally, Bokobza specifically identifies the method of Fisher and states that it had not solved the problem. Thus, Bokobza was aware of the method of Fisher. Yet Bokobza still stated that homogenous dispersion had not been achieved in polymers. Thus, Appellants have met from paragraph 7.66.04's burden with regard to Fisher.

**3. The Claimed Invention Solved this Problem and Was Heralded as a Major Breakthrough**

Finally, the claimed invention not only solved the problem of uniform dispersion, but it was widely heralded for doing so. The August 20, 2008 Declaration of Mr. Toru Noguchi stated that the inventors' work was published and received to great acclaim and fanfare at several different academic conferences. *See* August 20, 2008 Declaration of Mr. Toru Noguchi, item 11. The Declaration further states that Prof. Morinobu Endo, a world authority on carbon nanofibers, highly praised the novelty and effectiveness of the claimed material. *See* August 20, 2008 Declaration of Mr. Toru Noguchi, item 12. The Japanese Ministry of Economy, Trade and Industry also praised the claimed invention, and now funds research to further research and exploit the claimed material. *See* August 20, 2008 Declaration of Mr. Toru Noguchi, item 14. Mr. Toru Noguchi was offered (and accepted) a visiting professorship at National Shinshu University shortly after publishing his results. *See* August 20, 2008 Declaration of Mr. Toru Noguchi, item 13.

Thus, those of ordinary skill in the art acknowledged that the claimed invention had fulfilled a long felt need. Furthermore, the level of acclaim granted to the invention is presented as further evidence of both the desire in the field to achieve uniform dispersion, and the failure of those before to accomplish this feat.

For all these reasons, Appellants submit that the record shows that the claimed invention fulfilled a long felt, but unmet need in the field. As such, this rebuts the rejections presented in the Final Rejection.

\*\*\*\*\*

For at least the above reasons, the applied references fail to disclose or render obvious the features of independent claim 1, 7, 8, 27 and 28. Thus, withdrawal of the rejections of claims 1, 7, 8, 27 and 28 and claims 2, 3, 9, 10, 23, 24, 26 and 29 depending therefrom, is respectfully requested.

**VIII. CONCLUSION**

For all of the reasons discussed above, it is respectfully submitted that the rejections are in error and that the claims are in condition for allowance. For all of the above reasons, Appellants respectfully request this Honorable Board to reverse the rejections of claims 1-3, 7-10 and 23-29.

Respectfully submitted,



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Filed: October 28, 2009

**APPENDIX A - CLAIMS APPENDIX**

**CLAIMS INVOLVED IN THE APPEAL:**

1. A carbon fiber composite material comprising an elastomer and a plurality of carbon nanofibers substantially uniformly dispersed in the elastomer, wherein:  
  
the elastomer has an unsaturated bond or a group, having affinity to the carbon nanofibers;  
  
the elastomer in the composite material is in its uncrosslinked form; and  
  
the composite material has a first spin-spin relaxation time ( $T_{2n}$ ) of 100 to 3,000  $\mu\text{sec}$  and a second spin-spin relaxation time ( $T_{2nn}$ ) of being absent or 1,000 to 10,000  $\mu\text{sec}$ , and a fraction ( $f_{nn}$ ) of components having the second spin-spin relaxation time of less than 0.2, as measured under conditions of an observing nucleus of  $^1\text{H}$  at 150 °C by the Hahn-echo method using pulsed NMR technique.
2. The carbon fiber composite material according to claim 1, wherein the elastomer has a weight average molecular weight of 5,000 to 5,000,000.
3. The carbon fiber composite material according to claim 1, wherein the elastomer has, in at least one of its main chain, side chains and terminal chains, at least one member selected from the group consisting of a double bond, a triple bond, a carbonyl group, a carboxyl group, a hydroxyl group, an amino group, a nitrile group, a ketone group, an amide group, an epoxy group, an ester group, a vinyl group, a halogen group, a urethane group, a biuret group, an allophanate group, and a urea group.
6. The carbon fiber composite material according to claim 1, wherein the elastomer in the composite material is one of natural rubber (NR) and nitrile rubber (NBR).
7. A carbon fiber composite material comprising an elastomer and a plurality of carbon nanofibers substantially uniformly dispersed in the elastomer, wherein the elastomer in the composite material is in its uncrosslinked form, and the composite material has a first

spin-spin relaxation time ( $T_{2n}$ ) of 100 to 3,000  $\mu\text{sec}$  and a second spin-spin relaxation time ( $T_{2nn}$ ) of being absent or 1,000 to 10,000  $\mu\text{sec}$ , and a fraction ( $f_{nn}$ ) of components having the second spin-spin relaxation time of less than 0.2, as measured under conditions of an observing nucleus of  $^1\text{H}$  at 150 °C by the Hahn-echo method using pulsed NMR technique.

8. A carbon fiber composite material comprising an elastomer and a plurality of carbon nanofibers substantially uniformly dispersed in the elastomer, wherein the elastomer in the composite material is in its crosslinked form, and the composite material has a first spin-spin relaxation time ( $T_{2n}$ ) of 100 to 2,000  $\mu\text{sec}$  and a second spin-spin relaxation time ( $T_{2nn}$ ) of being absent or 1,000 to 5,000  $\mu\text{sec}$ , and a fraction ( $f_{nn}$ ) of components having the second spin-spin relaxation time of less than 0.2, as measured under conditions of an observing nucleus of  $^1\text{H}$  at 150 °C by the Hahn-echo method using pulsed NMR technique.

9. The carbon fiber composite material according to claim 1, wherein the elastomer in the composite material is in its uncrosslinked form and the composite material has a flow temperature higher than the inherent flowing temperature of the elastomer by 20 °C or more.

10. The carbon fiber composite material according to claim 1, wherein each carbon nanofiber has an average diameter of 0.5 to 500 nm.

23. The carbon fiber composite material according to claim 7, wherein the elastomer in the composite material is in its uncrosslinked form and the composite material has a flow temperature higher than the inherent flowing temperature of the elastomer by 20 °C or more.

24. The carbon fiber composite material according to claim 7, wherein each carbon nanofiber has an average diameter of 0.5 to 500 nm.

26. The carbon fiber composite material according to claim 8, wherein each carbon nanofiber has an average diameter of 0.5 to 500 nm.

27. A carbon fiber composite material comprising an elastomer and a plurality of carbon nanofibers substantially uniformly dispersed in the elastomer, wherein:

the elastomer has an unsaturated bond or a group, having affinity to the carbon nanofibers;

the elastomer in the composite material is in its crosslinked form; and

the composite material has a first spin-spin relaxation time ( $T_{2n}$ ) of its of 100 to 2,000  $\mu\text{sec}$  and a second spin-spin relaxation time ( $T_{2nn}$ ) of being absent or 1,000 to 10,000  $\mu\text{sec}$ , and a fraction ( $f_{nn}$ ) of components having the second spin-spin relaxation time of less than 0.2, as measured under conditions of an observing nucleus of  $^1\text{H}$  at 150 °C by the Hahn-echo method using pulsed NMR technique.

28. A carbon fiber composite material comprising an elastomer and a plurality of carbon nanofibers homogeneously dispersed in the elastomer, wherein the elastomer has an unsaturated bond or group bonding with an active part of each carbon nanofiber.

29. The carbon fiber composite material according to claim 28, wherein the unsaturated bond or group bonds with a terminal radical of each carbon nanofiber.

**APPENDIX B - EVIDENCE APPENDIX**

A copy of each of the following items of evidence relied on by the Appellants is attached:

The August 20, 2008 Declaration of Mr. Toru Noguchi. This evidence was entered into the record by the Examiner in the November 10, 2008 Office Action.

The May 7, 2009 Declaration of Mr. Toru Noguchi. This evidence was entered into the record by the Examiner in the August 14, 2009 Office Action.

Liliane Bokobza, Multiwall carbon nanotube elastomeric composites: A review. This evidence was entered into the record by the Examiner in the August 14, 2009 Office Action.

Thostenson, et al., Advances in the science and technology of carbon nanotubes and their composites: a review. This evidence is attached for the Board's consideration but is not in the record.

**APPENDIX C - RELATED PROCEEDINGS APPENDIX**

NONE





**PATENT APPLICATION**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**In re the Application of**

**Toru NOGUCHI et al.**

**Group Art Unit: 1794**

**Application No.: 10/821,175**

**Examiner: E. COLE**

**Filed: April 9, 2004**

**Docket No.: 127794**

**For: CARBON FIBER COMPOSITE MATERIAL AND PROCESS FOR PRODUCING  
THE SAME**

**DECLARATION UNDER 37 C.F.R. §1.132**

**I, TORU NOGUCHI, a citizen of Japan, hereby declare and state:**

1. I completed doctoral course in Materials Engineering at the Graduate School of Science and Technology of Kobe University in Hyogo, Japan in 1986 and a BS in Materials Engineering which was conferred upon me by Tohoku University in Miyagi, Japan in 1977.

2. I have been employed by Nissin Kogyo Co., Ltd since 2002 and I have over 5 years of work and research experience in elastomers and metal composite materials. I was employed by Misuboshi Belting Ltd., from 1986 to 2001, and I have a total of 15 years of work and research experience, mainly in elastomer technology.

3. I am a member of The Japanese Society of Polymer Science, the Japan Institute of Metals and The Japan Society of Applied Physics.

4. I am a named inventor in the above-captioned patent application.

5. I have a professional relationship with the assignee of the above-identified patent application. In the course of that professional relationship, I received compensation directly from the assignee for my work relating to Research and Development. I am being compensated for my work in connection with this Declaration.

6. I have extensive experience in, and knowledge of, the field of carbon fiber composite materials.
7. In the past to achieve high performance of a carbon fiber composite material it was necessary to mix large quantities of expensive carbon nanofiber into the elastomer to ensure sufficient carbon nanofiber presence in every portion of the material.
8. It was known in the field of carbon fiber composite materials that substantially uniform dispersion of carbon nanofibers in a carbon fiber composite material would create a composite material having advantageous properties.
9. Prior to the work of myself, and my co-inventors, a carbon fiber composite material having substantially uniform dispersion had not been achieved despite repeated attempts.
10. My co-inventors and I were the first to successfully fulfill this long felt, but unmet need in the field of carbon fiber composite materials.
11. Our work was published and received to great acclaim and fanfare and several different academic conferences.
12. Prof. Morinobu Endo, a world authority on carbon nanofibers, highly praised the novelty and effectiveness of the claimed material.
13. Shortly after publishing our results, I was offered (and accepted) a visiting professorship at Shinshu University, National University Corporation.
14. The Japanese Ministry of Economy, Trade and Industry praised the claimed invention and its novelty, and now funds research to further research and exploit the claimed material.
15. The Japanese Patent Office granted a patent on the claimed invention.

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date: August 20, 2008

Toru Noguchi  
Toru NOGUCHI



**PATENT APPLICATION**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Toru NOGUCHI et al.

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**DECLARATION UNDER 37 C.F.R. §1.132**

I, TORU NOGUCHI, a citizen of Japan, hereby declare and state:

1. I completed doctoral courses in Materials Engineering at the Graduate School of Science and Technology of Kobe University in Hyogo, Japan in 1986 and obtained a BS in Materials Engineering which was conferred upon me by Tohoku University in Miyagi, Japan in 1977.

2. I have been employed by Nissin Kogyo Co., Ltd since 2002 where I have over 5 years of work and research experience in elastomers and metal composite materials. I was employed by Mitsuboshi Belting Ltd., from 1986 to 2001, where I had a total of 15 years of work and research experience, mainly in elastomer technology. I am a Guest Professor, Institute of Carbon Science & Technology, Shinshu University.

3. I am a member of The Japanese Society of Polymer Science, the Japan Institute of Metals and The Japan Society of Applied Physics.

4. I am a named inventor in the above-captioned patent application.

5. I have a professional relationship with the assignee of the above-identified patent application. In the course of that professional relationship, I received compensation

directly from the assignee for my work relating to Research and Development. I am being compensated for my work in connection with this Declaration.

6. I have extensive experience in, and knowledge of, the field of carbon fiber composite materials.

7. I conducted a series of tests to determine the properties of composites made from carbon nanofibers (CNT) with ethylene propylene diene rubber (EPDM).

8. The purpose of the tests were to examine the effect that the method of mixing the components had on the final composite product.

9. In these tests the same raw materials were used. Specifically, in the experiments EPDM 100 parts by weight (phr) was used as the primary elastomer. Carbon nanofibers with an average diameter of 13nm in the amount of 10 phr and peroxide (DCP) 2 phr were used as crosslinking agents.

10. Each identical set of materials was mixed using one of three different mixing methods (methods A-C).

11. Mixing method A was a shear rolling method using the machine shown in the attached Fig. 1 (attached). Method A is the mixing method described in Applicants' specification. Two open rolls in a machine, capable of being cooled or heated between 5-120°C, were used. The rotation speed of the respective rolls could range from 1-30rpm.

12. In the test conducted using Method A, the EPDM was inserted between the rolls and placed around the rolls. CNT was mixed with the EPDM into the gap of the rollers at room temperature for 10 minutes. The temperature was then increased to 100°C for a further 10 minutes of mixing. Finally, the mixture was subjected to tight milling five times at 20°C with a roll distance of 0.1mm.

13. Mixing method B was a general mixing method using a Labo Plastmill (Banbury mixer style). This mixer is shown in the attached Fig. 2. This machine has two

rotors and a chamber that can be heated. The chamber has a volume of 370 ml and a material filling fraction of 65%.

14. In the test conducted using Method B, the EPDM and CNT were inserted between the two rotors in the chamber. The front was closed and the materials were mixed at a rotor rotational speed of 30rpm. Three mixing cycles were conducted. The composite was taken out of the chamber at a temperature of 180°C.

15. Mixing method C used a twin screw extruder, shown in attached Fig. 3. The extruder had a screw diameter of 30mm and a cylinder diameter of 32mm. The length of the cylinder was 1344mm. The screws could reach a rotational speed of 524 rpm.

16. In the test conducted using Method C, the slots of the twin screw extruder were heated to a cylinder temperature of 100°C. The materials were placed between the cylinder and the screw and then mixed for 10 minutes. Once mixing was completed the composite was extruded from the twin screw extruder at a temperature of 180°C and cooled.

17. The results of the tests are shown in Table 1.

18. The column labels in Table 1 are as follows:  $T_B$  is the dynamic storage modulus;  $E_B$  is the elongation at break.  $T_{2n}$  and  $T_{2nn}$  are the spin-spin relaxation times, and are well defined in Applicants' specification. Finally,  $F_{nn}$  is the fraction of components having the second spin-spin relaxation time, and is also well defined in Applicants' specification.

19. The attached Figures collectively labeled as Fig. 4 are morphology observations of the sample prepared in the above described experiments. Figs. 4A1-4A3 show the results using Method A. Figs. 4B1 and 4B2 show the results of Method B. Finally, Fig. 4C show the results of Method C.

20. Figs. 4B1 and 4C show "sea island" structures, while Fig. 4A1 does not. These figures share a common white scale of 100 $\mu$ m. The sea island structures can easily be seen in Fig. 4B1 and Fig. 4C. The sea island structures are not present in Fig. 4A1.
21. These sea island structures are aggregations of carbon nanofibers, ranging in size from ten to hundreds of micrometers wide. The sea area is the EPDM matrix and the island areas are CNT aggregations.
22. Mixing methods B and C result in dispersion of carbon nanofiber aggregations. But mixing methods B and C do not result in uniform dispersion of the carbon nanofibers themselves. By contrast, Method A results in uniform dispersion of the carbon nanofibers.
23. Table 1 shows that Method A results in a first spin-spin relaxation time of 1860  $\mu$ s and a second spin-spin relaxation time of 6100  $\mu$ s. These values lie in the range defined in claim 1.
24. Table 1 shows that Method B results in a first spin-spin relaxation time of 3200  $\mu$ s and a second spin-spin relaxation time of 12000  $\mu$ s. These values lie outside the range defined in claim 1.
25. Table 1 shows that Method C results in a first spin-spin relaxation time of 3900  $\mu$ s and a second spin-spin relaxation time of 17000  $\mu$ s. These values lie outside the range defined in claim 1.
26. As indicated above, the same raw materials were used in each test. In each test the final product was a reinforced piece of composite material. Yet the spin-spin relaxation times of each composite material were substantially different.
27. I therefore conclude that the spin-spin relaxation times of a carbon nanofiber reinforced elastomer varies, at least, with the mixing method.



28. I also conclude that general mixing methods, such as the two comparative mixing methods used (Methods B & C) disperse CNT aggregations but do not disentangle CNT aggregates to uniformly disperse the carbon nanofibers.

I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date:

May 7, 2009

Toru Noguchi  
TORU NOGUCHI

Attachments:

Table 1

Figs. 1-4

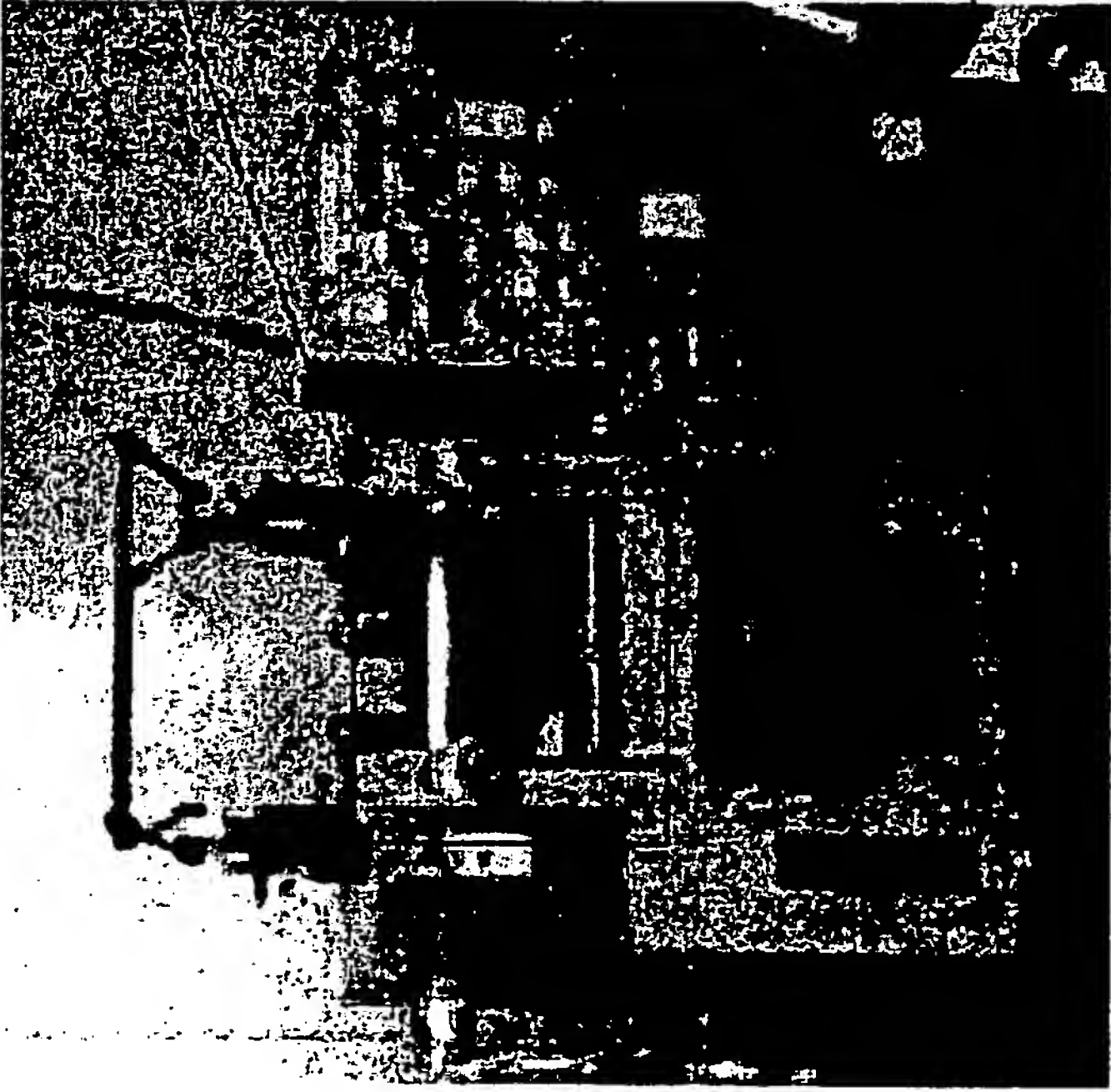


Fig. 1A

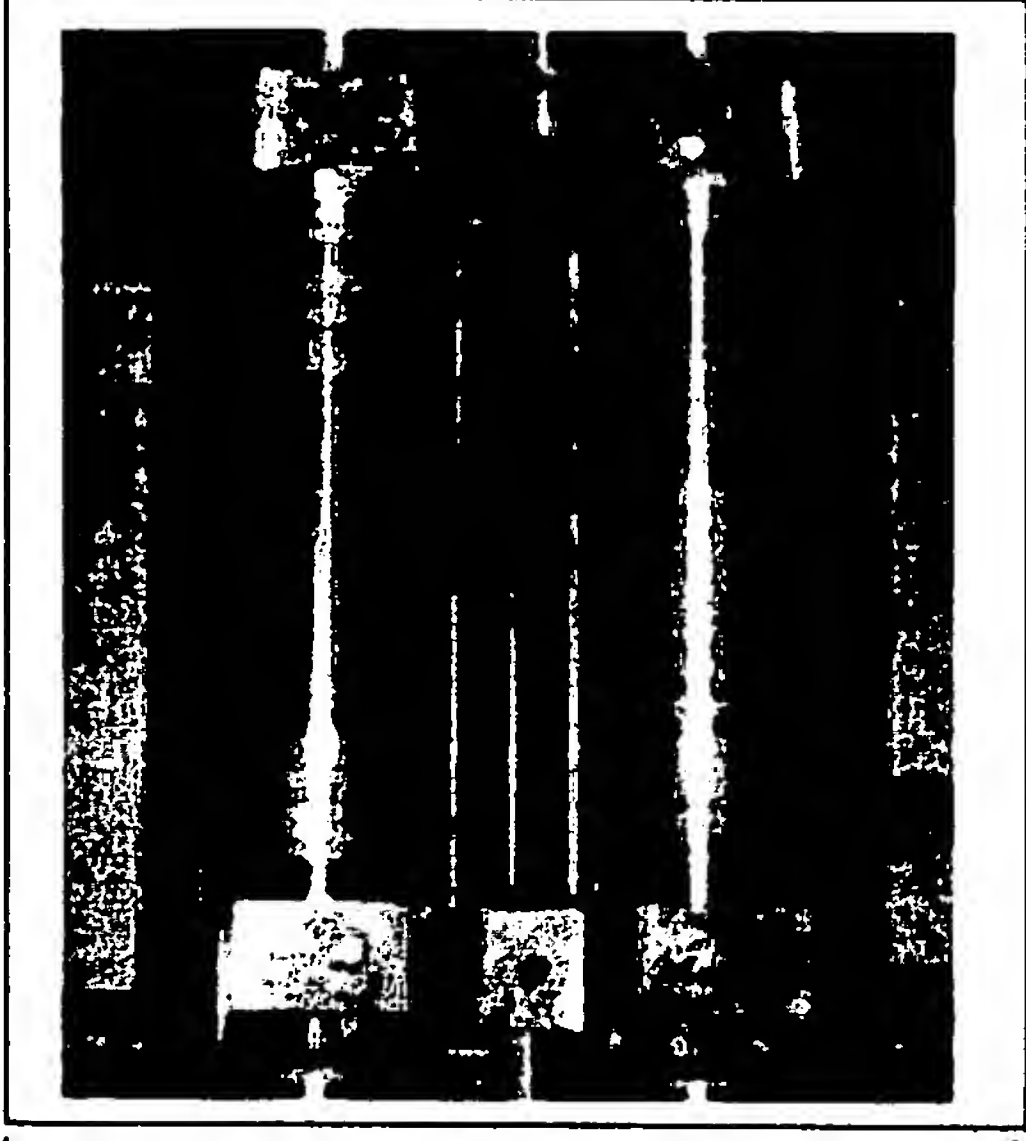


Fig. 1B

High-Power Open Rolls (Adjustable at Low Temperature Range)



Fig. 2A

Fig. 2B

Fig. 2C

Outer View

Rotors

Inner Chambers

Labo Plastmill: Brabender Plasticoder PL-2000 (Banbury Type)

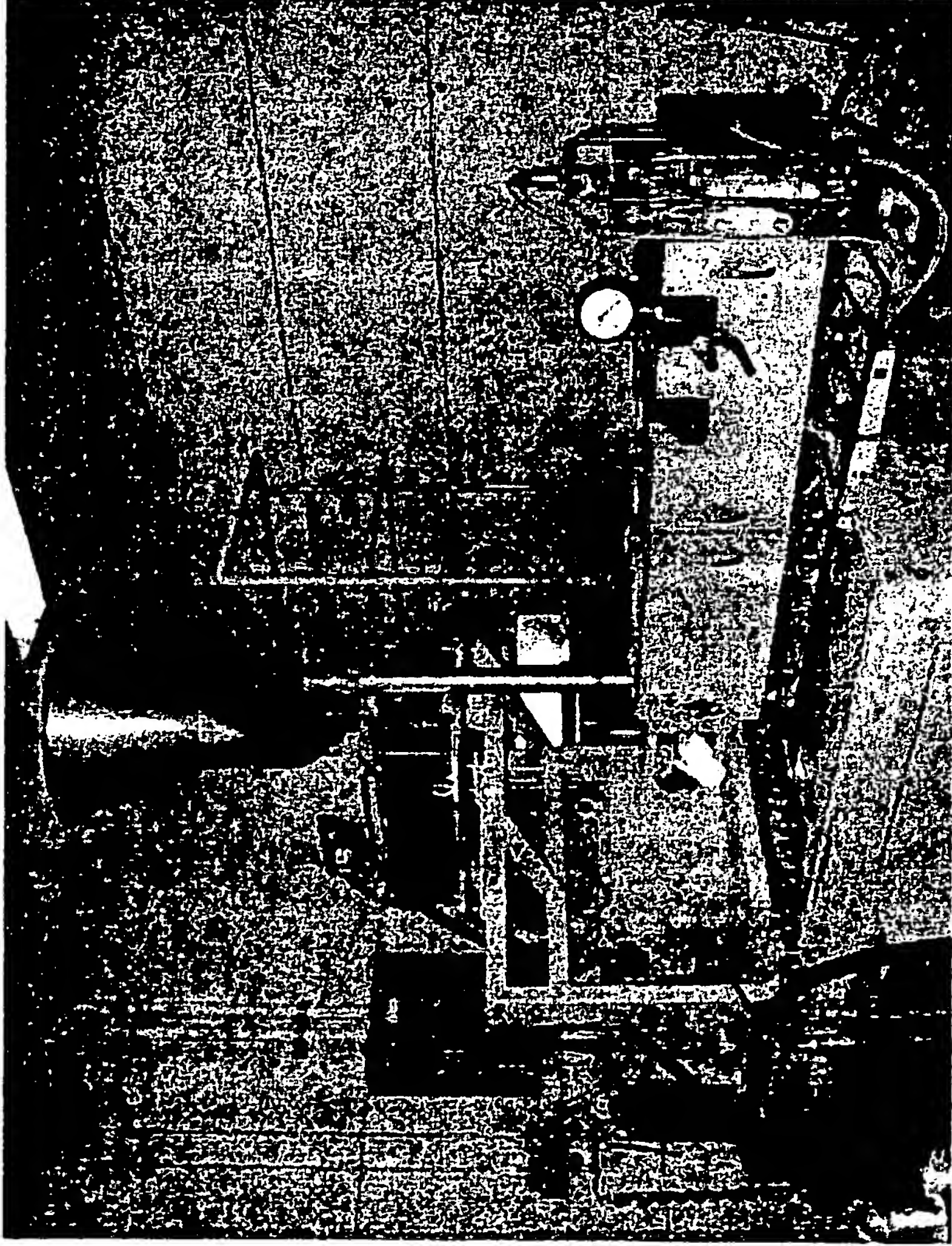


Fig. 3A

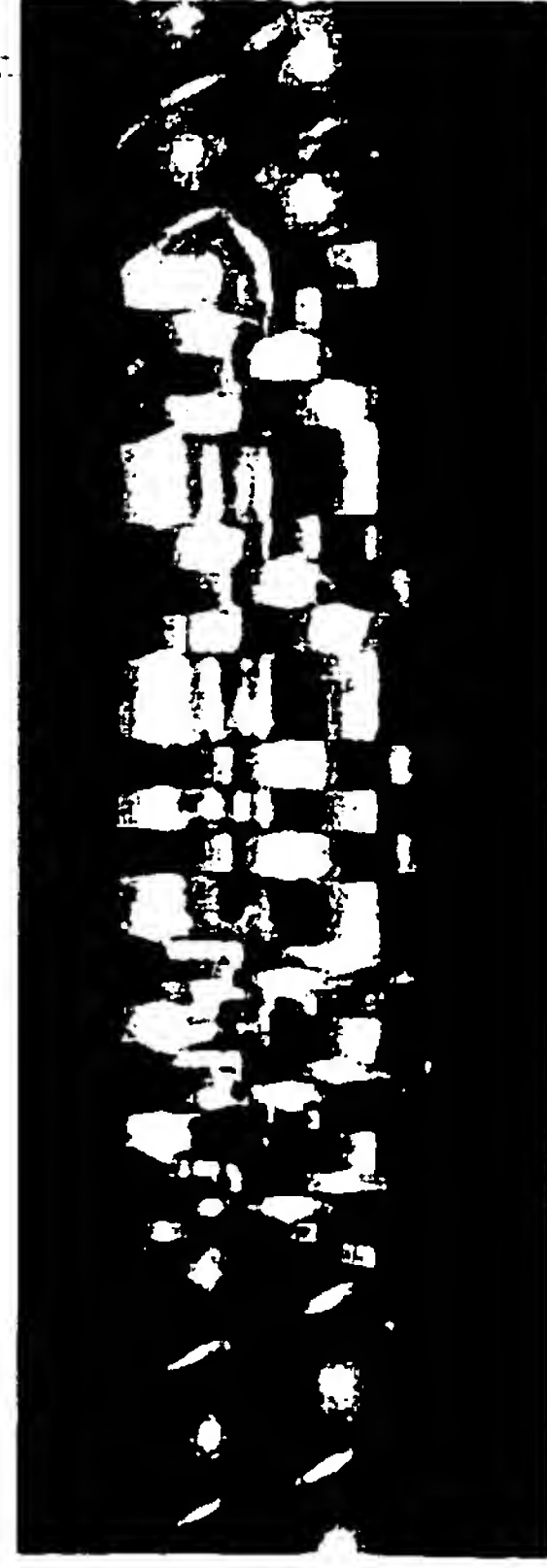


Fig. 3B

Overview of TEX30 $\alpha$  and Screw in Twin Screw  
Extruder (The Japan Steel Works, Ltd.)

Test Site: Industrial Technology Center of  
Okayama Prefecture

**Comparison of CNT/EPDM Composites prepared by  
Method A (Claimed Mixing Method) and General Mixing Methods B and C**

MIXERS	MIXING	HARDNESS	$T_B$ [MPa]	$M_{100}$ [MPa]	$M_{200}$ [MPa]	$E_B$ [%]	$T_{2n}$ (150°C) $\mu$ sec	$T_{2nn}$ (150°C) Msec	$F_{nn}$ (150°C)
METHOD A (Using Rolls)	Room Temp/10min +100°C/10min +20°C Tight milling observed 5times	66	7.1	3.4	5.4	207	1860	6100	0.18
METHOD B (Using Labo Plastmill)	100°C 3 Cycles (Temperature Rise of up to 180°C)	66	4.4	3.0	-	143	3200	12000	0.25
METHOD C (Using Twin Screw Extruder)	100°C 10min (Temperature Rise of up to 180°C)	65	4.8	3.1	-	151	3900	17000	0.31

TABLE 1



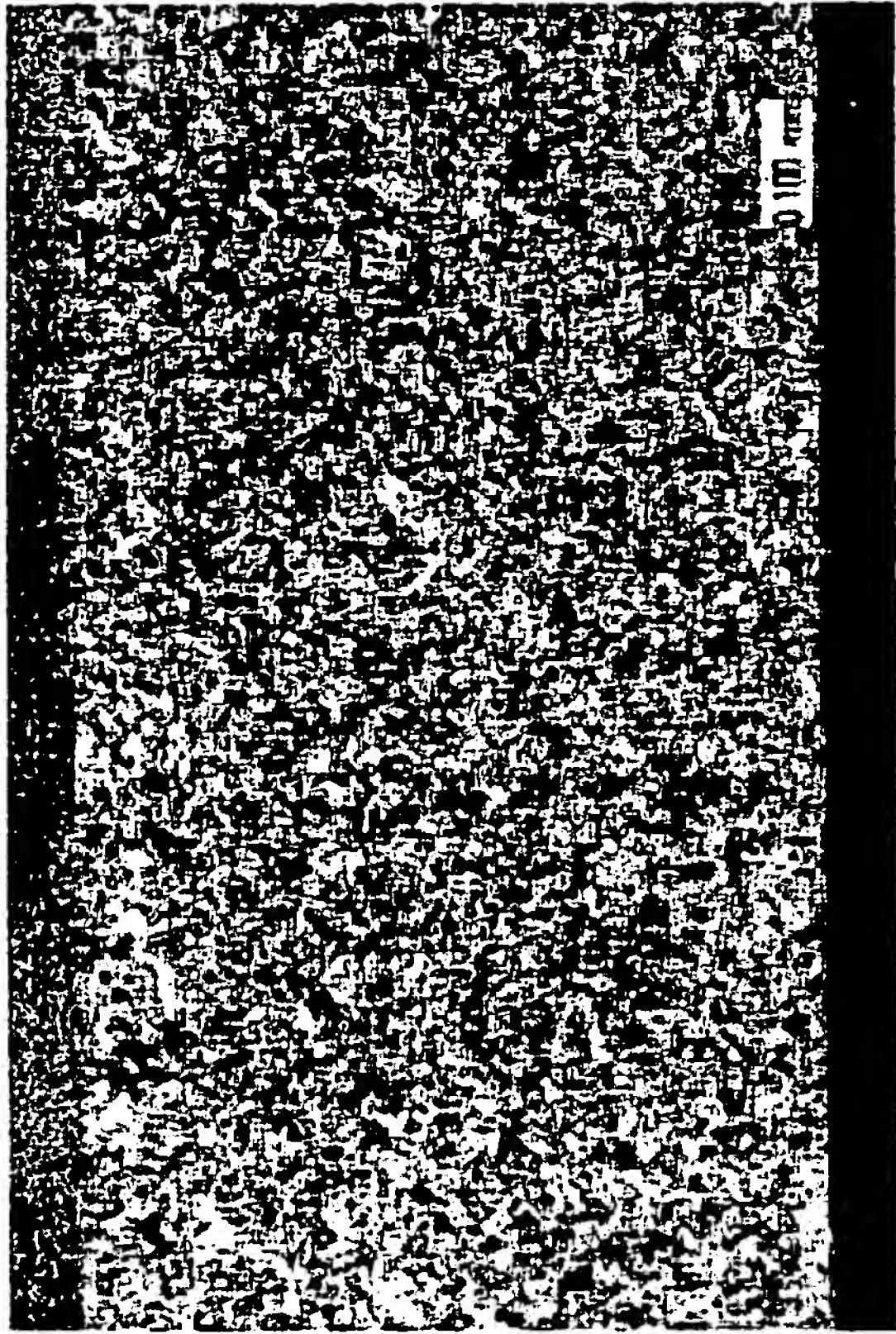


Fig. 4A1

Method A: Overview of Mix Sheet (Optical  
Microscopic Images; White Scale=100μm)  
Macro Uniform Dispersion



(A)SEM



Fig. 4A2

Method A: Enlarged View of TEM Image  
(Nano Uniform Dispersion)

Fig. 4A3

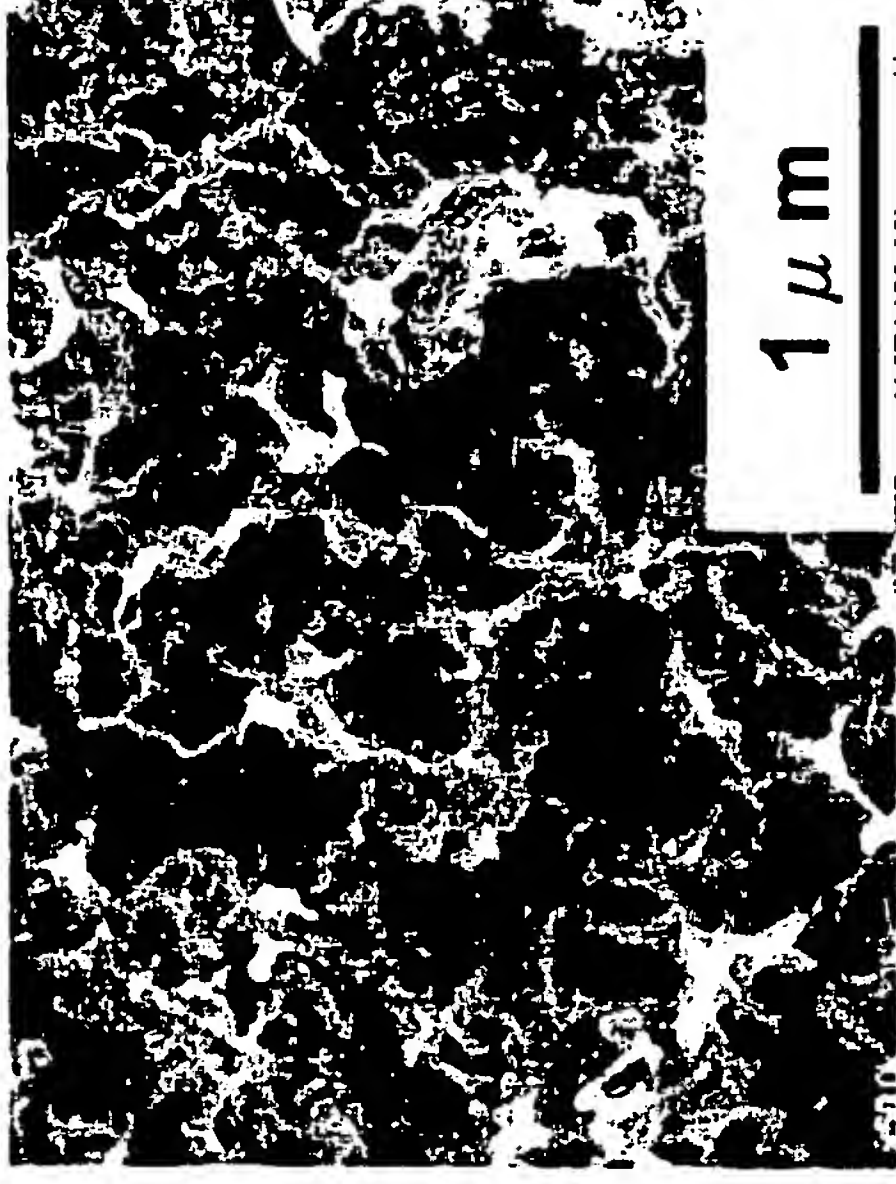
Method A: Enlarged View of SEM Image  
(Nano Uniform Dispersion)

Fig. 4B1



Method B: Overview of Mix Sheet (Optical Microscopic Images; White Scale=100 $\mu$ m)  
Macro Nonuniform Dispersion

Fig. 4B2



Method B: Enlarged View of SEM Image  
of Island-Shaped Portions

Method C: Overview of Mix Sheet  
(Optical Microscopic Images; White  
Scale=100 $\mu$ m)  
Macro Nonuniform Dispersion

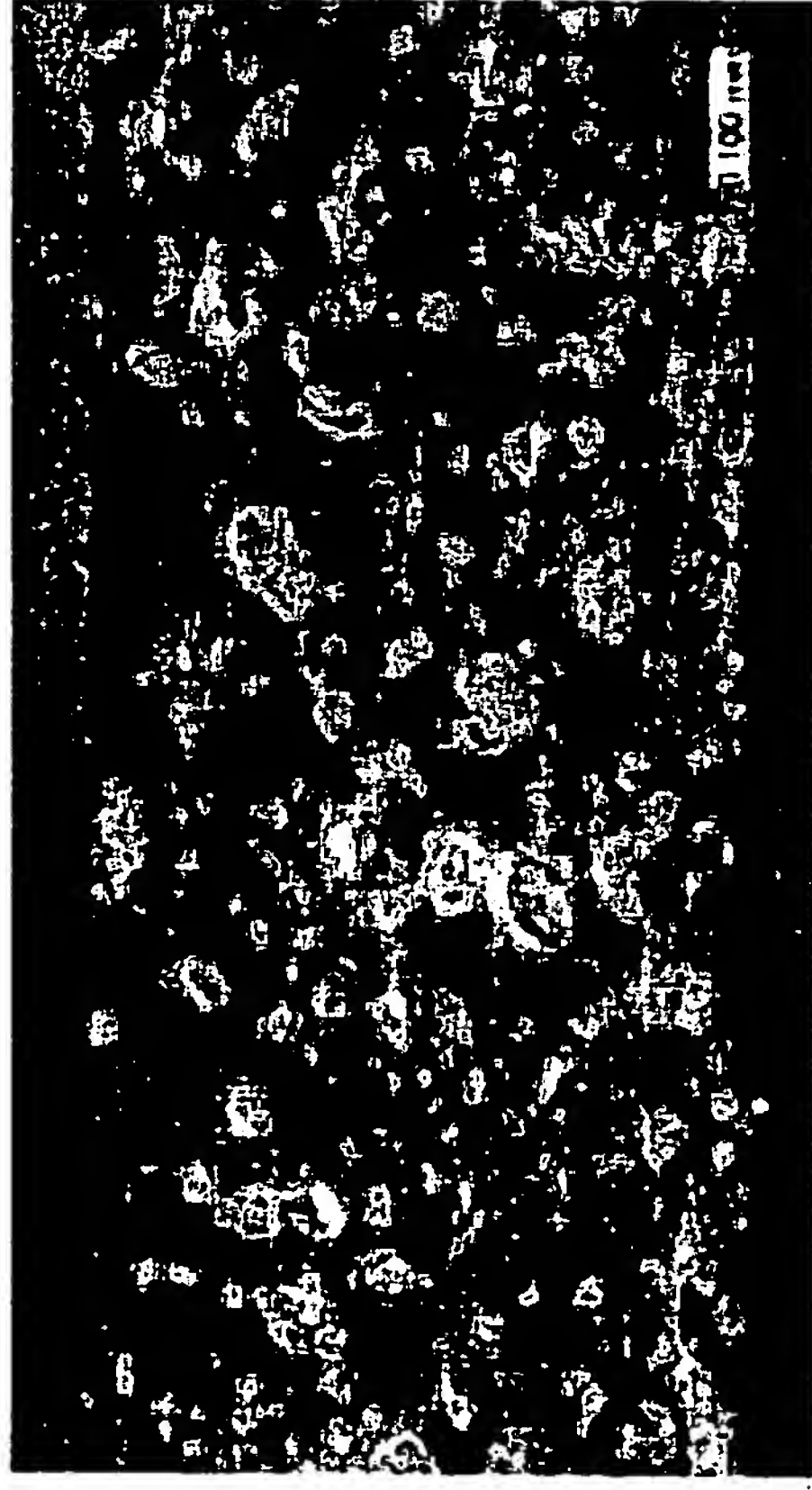
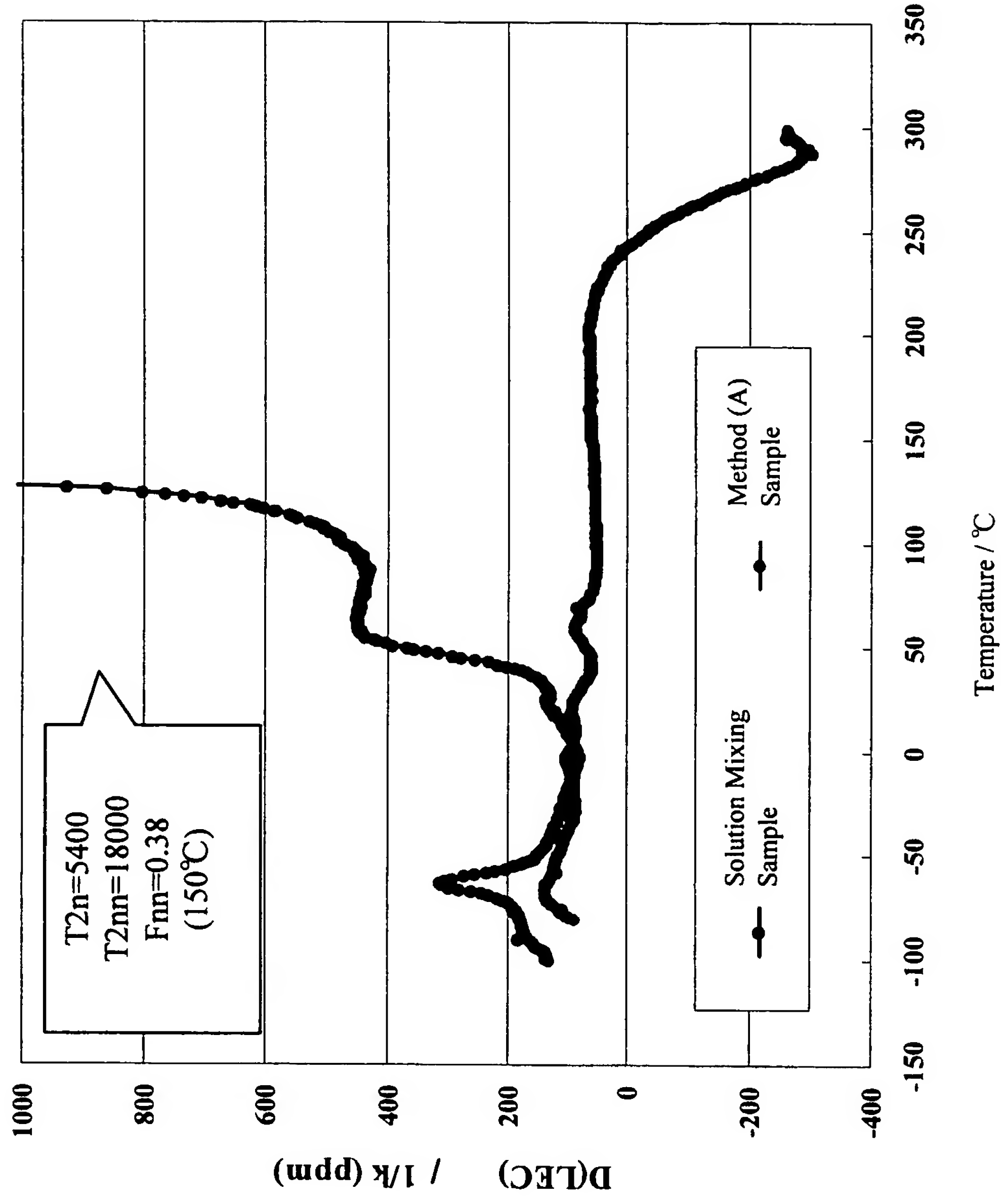


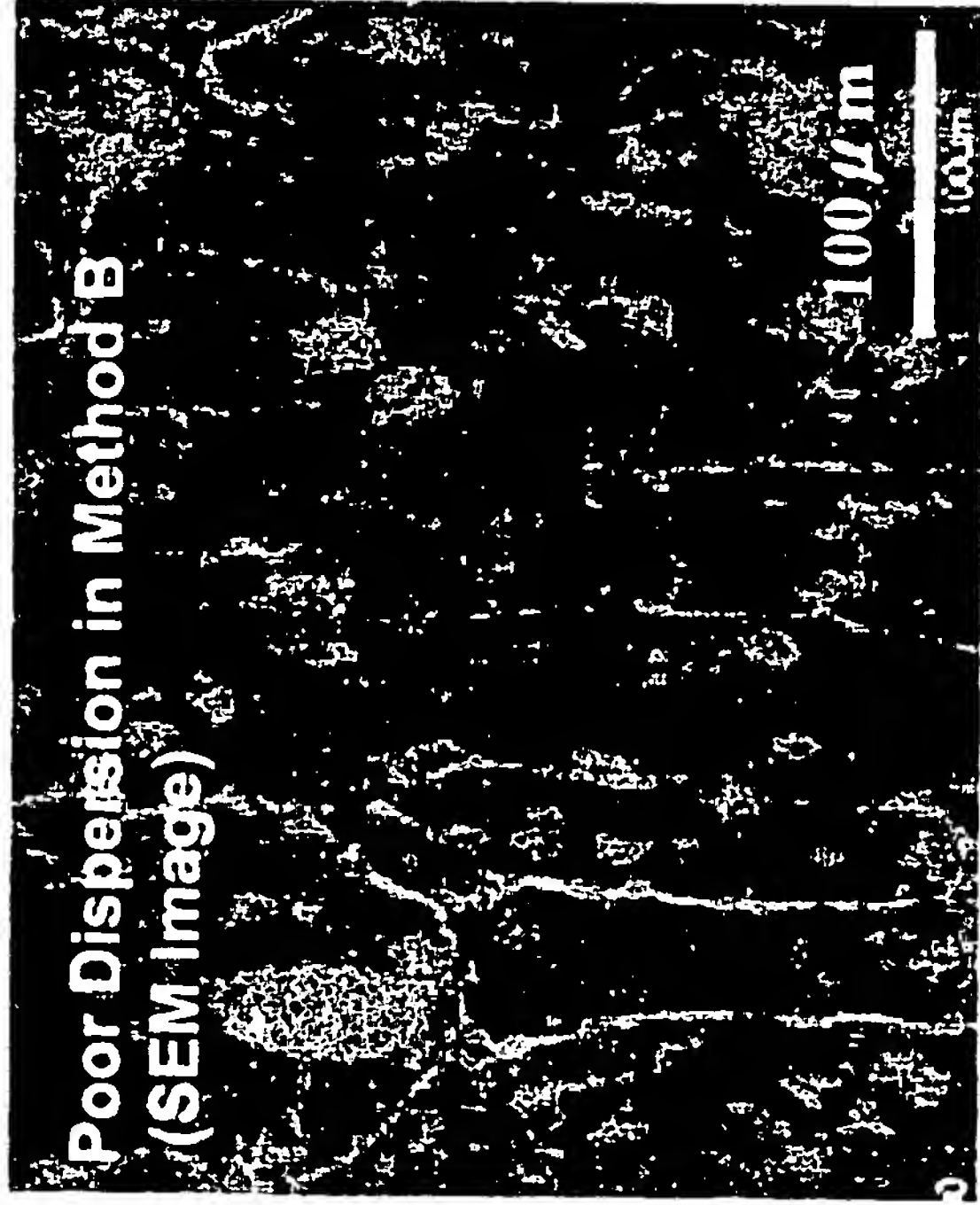
Fig. 4C





Differential Values for Linear Expansion Coefficient

Fig. 5



**Improved  
Dispersion**

- High-Speed Solution  
Agitation and  
Ultrasonic Agitation



Fig. 6

Improved Dispersion by Solution Mixing Method

## Feature Article

## Multiwall carbon nanotube elastomeric composites: A review

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**Abstract**

Nanostructured materials gained great importance in the past decade on account of their wide range of potential applications in many areas. A large interest is devoted to carbon nanotubes that exhibit exceptional electrical and mechanical properties and can therefore be used for the development of a new generation of composite materials. Nevertheless, poor dispersion and poor interfacial bonding limit the full utilization of carbon nanotubes for reinforcing polymeric media.

In this paper, recent advances on carbon nanotubes and their composites will be presented through results of the author's research, essentially based on filled elastomeric networks. The intrinsic potential of carbon nanotubes as reinforcing filler in elastomeric materials will be demonstrated. It will be shown that, despite a poor dispersion, small filler loadings improve substantially the mechanical and electrical behaviors of the soft matrix. With the addition of 1 phr of multiwall carbon nanotubes in a styrene–butadiene copolymer, a 45% increase in modulus and a 70% increase in the tensile length are achieved. Straining effects investigated by atomic force microscopy and infrared and Raman spectroscopies, provide interesting results for the understanding of the mechanical behavior of these nanotube-based composites. All the experimental data lead to the belief that the orientation of the nanotubes plays a major role in the mechanical reinforcement. The strong restriction in equilibrium swelling in toluene with the MWNT content is not ascribed to filler–matrix interfacial interactions but to the occlusion of rubber into the aggregates. On the other hand, carbon nanotubes impart conductivity to the insulator matrix. Between 2 and 4 phr, the conductivity increases by five orders of magnitude reflecting the formation of a percolating network. Changes in resistivity under uniaxial extension completed by AFM observations of stretched composites bring new insights into the properties of these composites by highlighting the contribution of orientational effects.

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**Keywords:** Carbon nanotubes; Elastomers; Reinforcement

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**1. Introduction**

Elastomers are usually reinforced with mineral fillers in order to get substantial improvements in strength and stiffness. The extent of property improvement depends on several parameters including the size of the particles, their aspect ratio, their degree of dispersion and orientation in the matrix and the degree of adhesion with the polymer chains [1].

The last few years have seen the extensive use of nanoparticles because of the small size of the filler and the corresponding increase in the surface area allowing to achieve the required mechanical properties at low filler loadings.

In order to create new material systems with superior properties, various nanoparticle morphologies have been used as reinforcing fillers in elastomeric matrices. These nanometer-scale reinforcing particles include spherical particles such as silica or titania [2–5], platelets such as layered silicates [6–12], carbon [13] or clay fibers [14] and multiwall or single-wall carbon nanotubes [15–17].

Sol–gel technique generating nano-sized silica or titania particles within a host matrix has proved to be an excellent approach for the synthesis of hybrid systems where the organic and inorganic components are intimately mixed into a new material exhibiting greatly improved mechanical properties.

Layered silicates have generated significant interest because they can give rise to exfoliated systems in which the individual silicate nanolayers are homogeneously and uniformly dispersed throughout the polymer matrix. The exfoliated

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nanocomposites exhibit significantly enhanced mechanical and physical properties when compared to unfilled polymers or conventional composites.

Since their discovery in 1991 [18], carbon nanotubes (CNTs) have attracted enormous attention for their fundamental behavior and for their use in a wide variety of applications in nanoelectronic devices [19–21], probe tips for scanning probe microscopes [22–26] or in the automotive and aerospace industries for the dissipation of electrostatic charges [27,28]. Owing to their structural characteristics and their electrical and mechanical properties, one of the most important opportunities in the future is the emergence of a new generation of composite materials since relatively low carbon nanotube loading (<10 wt.%) within polymeric matrices, are required for various applications [29,30].

## 2. Characteristics, synthesis methods and processing of carbon nanotubes for composite materials

Carbon nanotubes can be visualized as graphene layers rolled into cylinders consisting of a planar hexagonal arrangement of carbon–carbon bonds. Their outstanding properties are a consequence of this unique bonding arrangement combined with topological defects required for rolling up the sheets of graphite into cylinders. During growth, depending on the synthesis methods, they can assemble either as concentric tubes (multiwall nanotubes, MWNTs) or as individual cylinders (single-wall nanotubes, SWNTs). Their diameters range from about a nanometer to tens of nanometers with lengths ranging from several micrometers to millimeters or even centimeters.

Carbon nanotubes can be synthesized by different techniques including arc-discharge [31,32], laser ablation [33–36] and various catalytic chemical vapor deposition (CCVD) [37–40].

In the arc-discharge technique, an electric arc is generated between two graphite electrodes under a helium or argon atmosphere, which causes the graphite to vaporize and condense on the cathode. The deposit contains the nanotubes and also fullerenes, amorphous carbon materials and catalyst particles. This technique requires further purification to separate the CNTs from the by-products present in the crude material. The electrodes of graphite are doped with catalytic metal atoms (Ni, Co) for the production of SWNTs. A high-temperature pulsed arc-discharge technique has been developed for the synthesis of single- and double-wall (DWNTs) carbon nanotubes with narrower tube diameters than those obtained with the steady arc method [41,42].

In laser ablation, a laser ablates a graphite target in flowing argon at temperatures near 1200 °C. The graphite target contains a small amount of a metal catalyst such as nickel, cobalt, iron, platinum, yttrium. It has been shown that bimetallic catalysts are more productive than single metals. Various configurations of laser ablation experiments were developed for the production of single-wall carbon nanotubes. They range from a single or a dual pulsed laser to a continuous laser. The yield, mean diameter and diameter distribution can be

varied by varying the growth temperature, gas, pressure, catalyst composition, laser pulse, etc.

Small amounts of CNTs can be formed by arc-discharge and laser vaporization which is really a limitation to scale up production to the industrial level. Larger quantities of nanotubes can be obtained by the pyrolysis of a carbon source such as carbon monoxide, hydrocarbon gases (acetylene, ethylene, methane) or liquid aliphatic saturated hydrocarbons, over metal catalysts supported on silica, alumina or zeolite at temperatures between 500 and 1000 °C. The catalyst consists of nano-sized particles of a single metal (Fe, Co or Ni) or a mixture of metals. CCVD has been reported to be a low cost method in producing multiwall carbon nanotubes and nanotube bundles. Another interesting aspect is the ability to induce the tube growth in a given direction with a control of the dimensions affected by the experimental conditions (nature of the catalyst, type of support, carbon source, temperature).

Composites obtained by dispersing nanotubes into different polymeric matrices have attracted wide attention in order to develop ultra-lightweight and extremely strong materials. In polymer composites, filler dispersion as well as interfacial interactions have been shown to be crucial parameters for enhanced mechanical properties. In fact, one of the biggest challenges is to obtain a homogeneous dispersion of carbon nanotubes in a polymer matrix because van der Waals interactions between individual tubes often lead to significant aggregation or agglomeration, thus reducing the expected property improvements of the resulting composite. But to date, despite the fact that much progress has been made in the processing techniques, the mechanical improvement brought about by incorporation of nanotubes remains minor with regard to the potential based on the properties of the nanotube itself. A review of Thostenson et al. [43] and Moniruzzaman and Winey [44] illustrates the significant challenges that must be overcome before the potential is realized.

Different techniques to attempt to optimize the nanotube dispersion within the polymeric medium have been used. They include solution mixing [45], sonication [46,47], coagulation [48], melt compounding [49–51], in situ miniemulsion polymerization [15,52,53], oxidation [54] or chemical functionalization of the tube surface [55–57], use of surfactants [58]. The ultimate goal of these processing conditions is to separate the individual nanotubes in order to get a homogeneous dispersion throughout the matrix while the chemical functionalization is intended to bring some adhesion between the nanotubes and the polymer thus enabling effective stress transfer at the polymer–filler interface.

Various strategies for chemical functionalization of carbon nanotubes have already been reported. They involve covalent or noncovalent attachments of functional groups in order to improve solubility and processability of CNTs in organic media. The use of ball milling in specific atmosphere allowed the introduction of functional groups such as thiol, amine, amide, chloride, carbonyl, thiomethoxy and acyl chloride, onto carbon nanotubes [59]. Functionalization of SWNTs via electrochemical reduction of a variety of aryl diazonium salts was described [60]. Functionalization can also be carried out



through oxidation of the nanotubes to induce formation of carboxylic, carbonyl or hydroxyl groups to nanotube end-caps or sidewalls. These functionalities serve as anchoring sites and open the way to further derivatization reactions that made the nanotubes soluble in organic solvents. For example, CNTs functionalized by oxidizing acid treatment can be submitted to fluorination and subsequent derivatization or to amine reactions with alkylcarboxyl groups attached to the nanotubes [61–64]. These types of approaches were successfully applied for the synthesis of epoxy matrices in which the nanotubes were integrated into the structure of the epoxy system through the sidewall amino functional groups [62,63]. Water-soluble SWNTs, interesting for chemical and biomedical applications, were also obtained by grafting glucosamine after producing acyl chloride on acid-treated nanotubes [65].

Functionalization via vigorous oxidation processes followed by covalent bonding has been shown to introduce defect sites within the nanotube structure where  $sp^2$  hybridization is converted to  $sp^3$  hybridization, which may affect the properties of the nanotube itself [66]. Electrochemical modification [67,68], surface-initiated polymerization in which polymer chains are covalently coupled onto the CNT surface which bears polymerization initiators [69–71] have been used to minimize damage of CNTs. On the other hand, shortening and mechanical damage such as buckling, bending and dislocations in the carbon structures were also induced by the sonication technique used to disperse the CNTs [72,73]. Shortening the nanotubes could be detrimental since it reduces the high aspect ratio which is one of the potential advantages of the nanotubes for their use as reinforcing fiber in polymer matrices.

### 3. Characterization of carbon nanotubes

The morphology and state of dispersion of the carbon nanotubes in a polymer matrix can be investigated using transmission electron microscopy (TEM) and atomic force microscopy (AFM).

Shown in Fig. 1 are typical TEM images of a toluene suspension of multiwall carbon nanotubes (MWNTs) previously sonicated before being put onto copper grids for observation (Fig. 1A–D). Fig. 1A reveals a broad distribution in lengths and diameters which are in the range of 0.1–5  $\mu\text{m}$  and 10–50 nm, respectively, and Fig. 1B shows the curled structure of an individual tube. The nanotubes can be highly entangled with one another and form an interconnecting structure (Fig. 1C). Fig. 1D magnifies the nanostructure of a multiwall carbon nanotube with several layers of graphitic carbon and a hollow core.

Fig. 1E–H shows the TEM images of composite based on styrene–butadiene rubber (SBR) filled with 4 phr of MWNTs (phr = parts per hundred parts of rubber). Bundled MWNTs can be clearly identified in Fig. 1E. Individual nanotubes are visualized in Fig. 1F and G and black spots correspond to aggregates. A magnification of one bundle (Fig. 1H) shows an orientation of nanotubes occurring probably during hot

pressing of the film. This orientation is expected to play a role in mechanical reinforcement.

TEM images were obtained on a JEOL 100CXII. Pure carbon nanotubes were sonicated in toluene and droplets of the suspension were put onto copper grids for observation. Ultra-thin films (60 nm thick) of the composite samples were cut by means of an ultramicrotome LEICA ULTRACUT UCT cooled at  $-80^\circ\text{C}$  by liquid nitrogen and put onto copper grids.

Additional information on how the nanotubes are actually being distributed within the polymer matrix can be obtained from atomic force microscopy. AFM has been shown to be particularly well suited for the characterization of filled elastomers and more generally of heterogeneous systems with components of different stiffness [74].

AFM images of SBR filled with 10 phr of MWNTs, shown in Fig. 2, give some indication of a larger scale dispersion than that given in Fig. 1. The brighter domains easily identified and rather homogeneously distributed in the film, are ascribed to filler aggregates. It has to be recalled that topography and error signal reveal surface roughness while phase imaging, which provides variation of surface stiffness, is particularly useful in elastomeric composites filled with carbon nanotubes on account of huge differences in moduli between the two components.

AFM investigations were performed with a Thermomicroscope CP Research System, using tapping mode and phase imaging. Topography, error signal and phase images were simultaneously recorded in order to get a topographic and compositional mapping of the surface.

### 4. Mechanical properties of nanotube-based elastomeric composites

Conventional fillers such as carbon black or silica, when added to elastomeric systems usually cause an increase in the modulus involving a hydrodynamic effect arising from the inclusion of rigid particles and an increase in the cross-linking density created by polymer–filler interactions [75–81].

The anisometry of particle aggregates or agglomerates is also expected to increase the modulus as well as the occluded rubber, considered as a typical mechanical interaction and consisting of elastomer chains trapped inside the filler aggregates. This occluded rubber, which is assumed to be partially shielded from deformation, increases the effective filler concentration.

The extent of filler agglomeration has a marked influence on the low strain dynamic properties of filled vulcanizates. While unfilled elastomers display little changes in dynamic properties upon increasing strain amplitude, the storage modulus of filled systems decreases significantly showing a typical non-linear behavior known as the Payne effect [82]. A large amount of work has been reported on this effect but the most accepted interpretation is the gradual breakdown of the filler network or filler “networking” as denominated by Wang [83], with increasing strain amplitude. In his paper reviewing the effect of filler characteristics on dynamic properties in connection with processing conditions and additives,



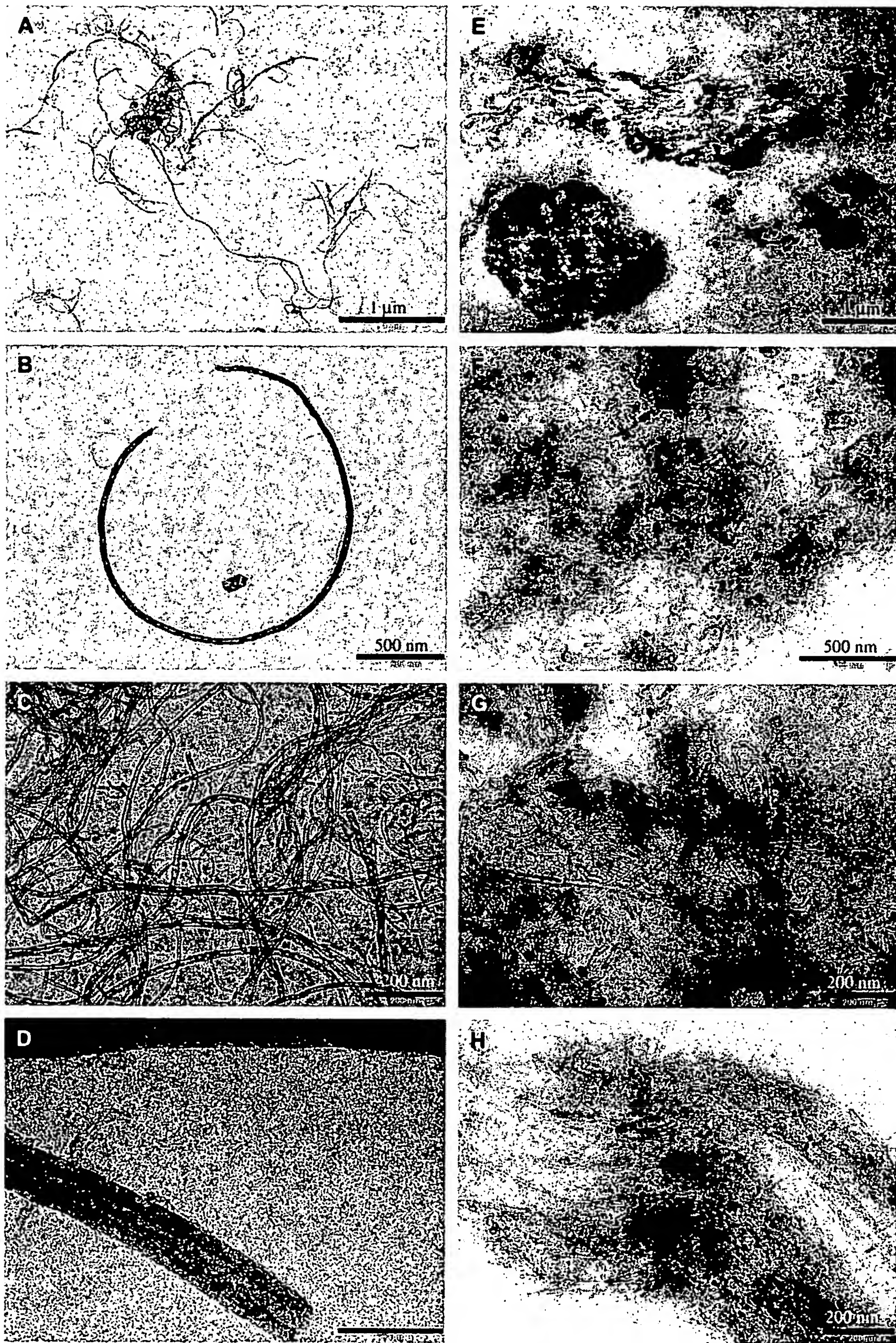


Fig. 1. TEM images. A–D: pure MWNTs; E–H: SBR/4 phr MWNT composite.

Wang demonstrates that the formation of the filler network is not only the result of filler–filler interactions but also of polymer–filler and polymer–polymer interactions. Nevertheless

any processing method improving dispersion and avoiding the formation of direct inter-particle contacts or increasing the polymer–filler interactions will depress filler networking.



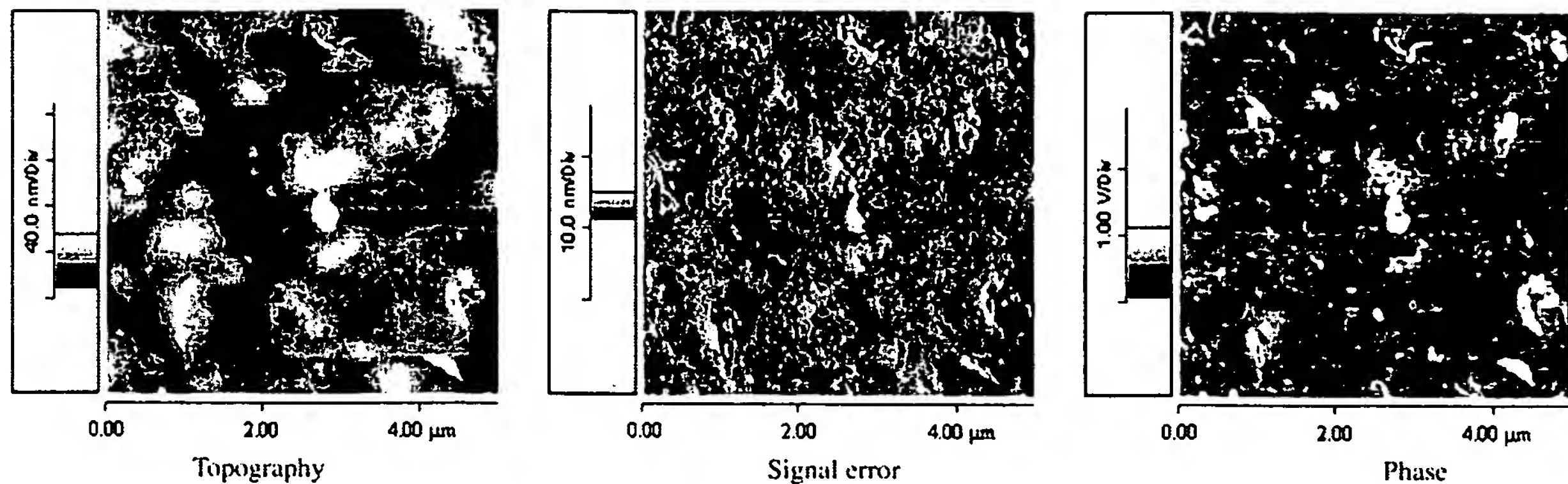


Fig. 2. AFM images of SBR filled with 10 phr of multiwall carbon nanotubes (MWNTs).

Also related to reinforcement is the stress-softening effect called the “Mullins effect”, observed at high extensions and characterized by a pronounced lowering in the stress when the filled vulcanizate is extended a second time [84]. This process, which can be considered as a hysteretic mechanism related to energy dissipated by the material during deformation, corresponds to a decrease in the number of elastically effective network chains. It results from chains that reach their limit of extensibility by strain amplification effects caused by the inclusion of undeformable filler particles [85,86]. Stress-softening in filled rubbers has been associated with the rupture properties and a quantitative relationship between total hysteresis (area between the first extension and the first release curves in the first extension cycle) and the energy required for rupture has been derived [87,88].

On account of their extremely high moduli, carbon nanotubes are expected to provide much higher reinforcement effects than conventional fillers. By using an atomic force microscope, Salvétat et al. [89] measured elastic moduli of SWNTs around 1 TPa and with a technique based on electrically induced mechanical deflections of MWNTs in a transmission electron microscope, instead of; elastic bending modulus was found to decrease sharply (from about 1 to 0.1 TPa) with increasing diameter (from 8 to 40 nm) [90]. On the other hand, tensile strengths of individual MWNTs were measured with a “nanostressing stage” located within a scanning electron microscope [91]. It was shown that the MWNTs broke in the outermost layer and the tensile strength of this layer ranged from 11 to 63 GPa while the Young’s modulus varied from 270 to 950 GPa.

Significant improvements in mechanical properties of polymeric matrices by CNT addition have been reported. Allaoui et al. [92] found that the incorporation of 1 wt.% of MWNTs into an epoxy matrix results in an increase in the Young’s modulus and in the yield strength by, respectively, 100 and 200% compared to the pure matrix. Reinforcement effects were also observed by adding MWNTs in phenolic resins [93,94] and in polystyrene [95]. Nevertheless, in polyethylene composites, McNally et al. [96] observed a decrease in the ultimate tensile strength and elongation at break with addition of MWNTs suggesting poor interfacial interactions between the MWNTs and the polymer matrix.

Some studies also report the use of CNTs in elastomeric matrices. SWNTs [17] and MWNTs [97] were incorporated in natural rubber. In the first paper, the reinforcing effect of the nanotubes is revealed by a dynamic mechanical analysis showing an increase in the storage modulus. In the second paper, tensile strength, tensile modulus and toughness are shown to increase with the filler loading while the elongation at break decreases. Tensile tests performed on a silicone rubber mixed with SWNTs also display dramatic improvement in the mechanical properties as a function of filler content [16]. The initial modulus increase has been shown to be approximately linear with weight fraction, with a slope of 200%/wt.%.

We have investigated the effect of incorporation of multiwall carbon nanotubes (MWNTs) into elastomeric matrices. The level of reinforcement is assessed through a mechanical characterization as a function of nanotube loading.

Fig. 3 shows, as a typical example, stress–strain curves for a pure styrene–butadiene rubber (SBR) and for MWNTs/SBR composites and the experimental mechanical properties are listed in Table 1. The styrene–butadiene rubber contains

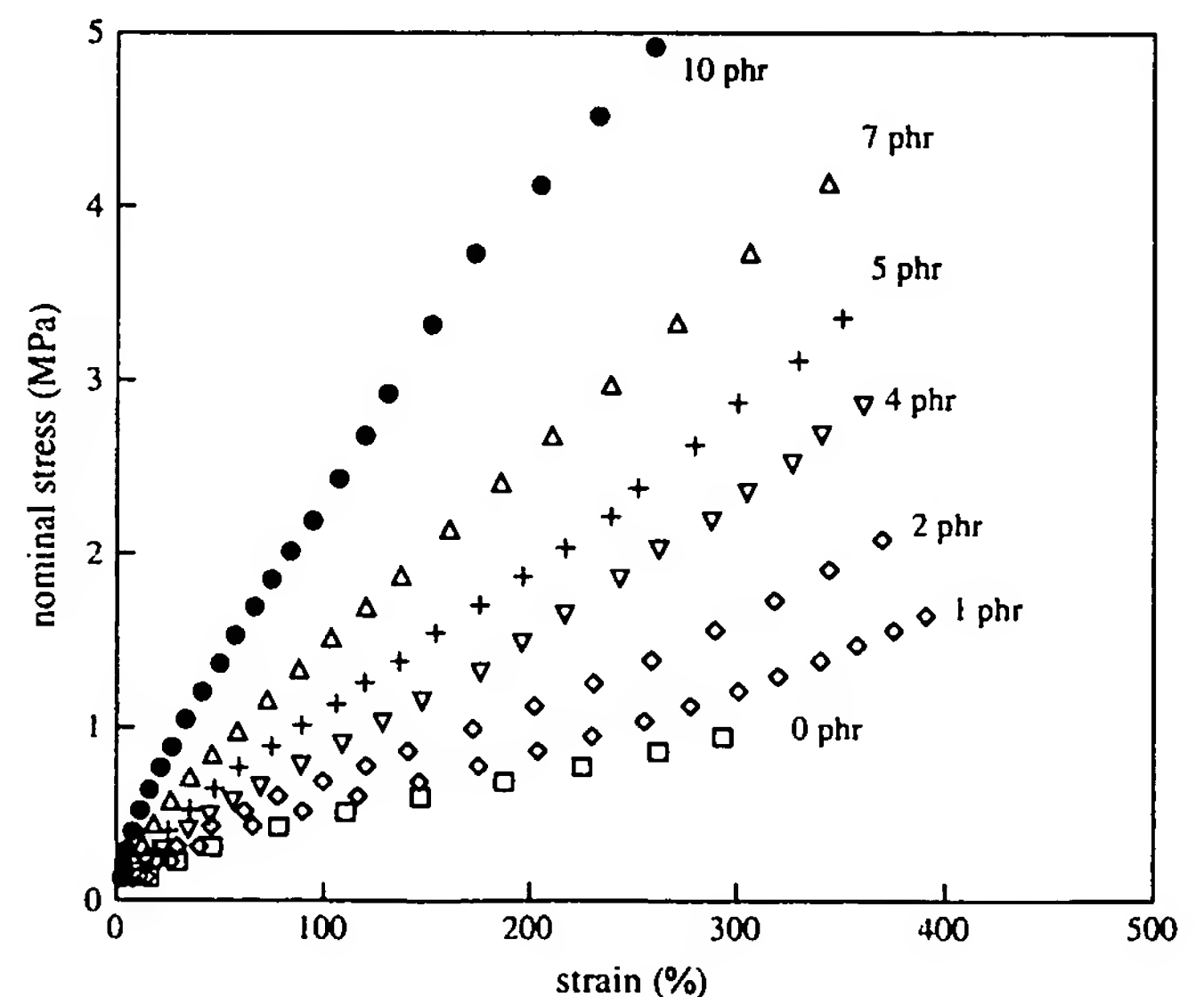


Fig. 3. Stress–strain curves for pure SBR and MWNT/SBR composites. The filler content is expressed in phr (phr = parts per hundred parts of rubber).



Table 1  
Mechanical properties of SBR and SBR composites

Filler loading (phr)	$E$ (MPa)	Stress at 100% (MPa)	Stress at 200% (MPa)	Stress at 300% (MPa)	Stress at break (MPa)	Strain at break (%)	$Q_{\text{rubber}}$
0	0.24	0.49	0.71	0.96	0.95	300	6.54
1	0.35	0.55	0.85	1.21	1.64	390	5.99
2	0.43	0.70	1.10	1.62	2.08	370	5.59
3	0.59	0.89	1.46	2.11	3.13	420	4.92
4	0.61	0.86	1.51	2.32	2.85	360	4.83
5	0.73	1.11	1.89	2.84	3.36	350	4.64
7	0.93	1.48	2.54	3.67	4.14	350	3.81
10	1.40	2.44	3.91	—	4.92	260	3.15

$Q_{\text{rubber}}$  represents the equilibrium swelling ratio of the rubber phase in toluene.

25 wt% of styrene units. The microstructure of the butadiene phase is the following: 10% *cis*, 17% *trans*, 73% 1,2.

The strain–stress measurements were carried out at room temperature on strips of  $50 \times 5 \times 0.2 \text{ mm}^3$  between two clamps by means of a sequence of increasing weights attached to the lower clamp. The distance between two marks on the sample was measured with a cathetometer after allowing sufficient time (10 min after adding a weight) for equilibration.

Clearly there is reinforcement as evidenced by considerable improvements in stiffness and tensile strength of the composites with the filler loading. With the addition of only 1 phr of MWNTs (phr = parts per hundred parts of rubber), a 45% increase in elastic modulus and a 70% increase in the tensile strength are achieved. The slight reduction in the ultimate strain observed for the sample filled with 10 phr of MWNTs with regard to the pure polymer may result from the presence of aggregates increasing with the filler content.

As these systems are submitted to sulfur vulcanization, SH-functionalized MWNTs were also used in order to determine whether the grafted groups are involved in the vulcanization process, thus bringing some adhesion between the organic and inorganic phases. No further improvement in the mechanical properties is gained with regard to the results obtained with untreated carbon nanotubes which is probably due to the small degree of nanotube functionalization which is around 1%. In a recent paper of Miltner et al. [98] dealing with nanocomposites based on ethylene–vinyl acetate copolymer in combination with several types of organoclay or carbon nanotubes, chemically functionalized carbon nanotubes bearing acetate or hydroxy moieties at their surface are seen to display less interactions than clay-filled systems at similar loading. The authors also mention the limited degree of surface functionalization.

The extent of reinforcement depends on several filler characteristics such as its modulus, geometry and orientation within the host matrix [99,100]. The extremely high modulus of carbon nanotubes (the value of 1 TPa is usually reported in the literature) may provide composites with mechanical properties that exceed those of any previously existing materials. On the other hand, according to theories and models describing the tensile behavior of filled composites, fibers are the most efficient at enhancing stiffness [101]. In order to take advantage of the full potential of carbon nanotubes for any given application in polymer nanocomposites and to understand their

superior efficiency as reinforcing fillers, it is interesting to compare the experimental data with theoretical models intended to predict the properties of composite materials. The Guth model [102] only based on the aspect ratio,  $f$ , and volume fraction,  $\phi$ , of filler, has been widely used to account for the change in modulus in filled elastomers:

$$E = E_0(1 + 0.67f\phi + 1.62f^2\phi^2), \quad (1)$$

$E$  and  $E_0$  are the moduli of the composite and the unfilled elastomer, respectively.

The Halpin–Tsai model [103] also predicts the stiffness of the composite as a function of the aspect ratio. The longitudinal modulus measured parallel to perfectly oriented fibers is expressed in the general form:

$$E = E_0(1 + 2f\phi\eta)/(1 - \phi\eta) \quad (2)$$

where  $\eta$  is given by

$$\eta = [(E_f/E_0 - 1)/(E_f/E_0 + 2f)] \quad (3)$$

$E_f$  being the modulus of the filler.

In elastomeric composites,  $E_f \gg E_0$ , so Eq. (2) reduces to

$$E = E_0(1 + 2f\phi)/(1 - \phi) \quad (4)$$

In Fig. 4, the experimental values of  $E/E_0$  are compared with the Guth and Halpin–Tsai predictions using the respective aspect ratios of 40 and 45 to fit the data. While the Guth model departs from the experimental results at the highest filler loadings, the Halpin–Tsai model, for perfectly aligned fibers, shows good agreement within the volume fraction range investigated. It is interesting to mention that both models yield almost similar aspect ratios. The values required to fit the experimental data are lower than that calculated from the average dimensions of the MWNTs. It is most probably due to aggregation of the nanotubes which reduces the aspect ratio of the reinforcement.

As already mentioned, nanotube alignment occurring, partially during film processing or, of course during stretching, has to be taken into account in the mechanical behavior of the composites. Phase-contrast tapping-mode AFM imaging of silica-filled elastomers under uniaxial stretching has greatly improved our molecular understanding of rubber reinforcement [104]. AFM observation of carbon nanotube-filled SBR was also carried out in order to have a look at the behavior

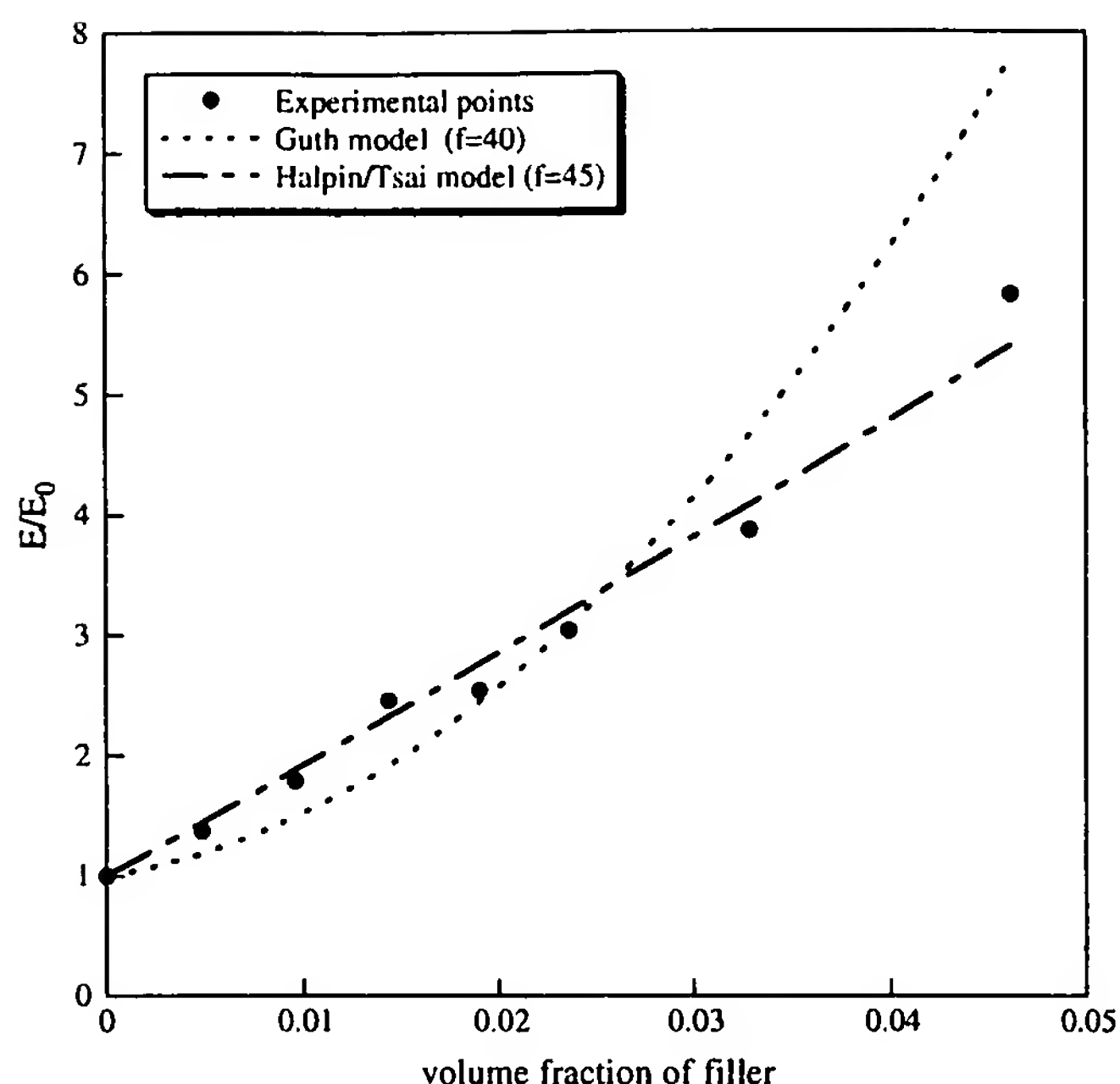


Fig. 4. Experimental moduli plotted versus volume fractions of MWNTs and comparison with theoretical predictions.



Fig. 5. Stretching device for AFM experiments.

of filler aggregates upon application of a macroscopic strain and also after suppression of the strain and second stretching. The sample (around 200  $\mu\text{m}$  thick) was put on a small stretching device specially fitted to the sample holder of the multi-mode AFM (Fig. 5). The deformation is maintained, thanks to the clamps screwed in the body of the device. The strain can be evaluated from the measurement of the distance between the two ink lines drawn on the surface of the film.

Phase images of films stretched to extension ratio (ratio of the length of the sample in the direction of strain to the initial length before deformation) equal to 1.8 and then 2.8 are shown in Fig. 6 for the 10 phr filled composite. Applying a uniaxial deformation to the sample results in orientation of the filler aggregates appearing as white areas. At the highest elongation, the bundles can be seen to be broken up into long straight structures. A quite different morphology is obtained after relaxation of the sample to the unstressed state (Fig. 7a) which is in fact more deformed than the original material on account of the permanent deformation exhibited by filled elastomers. In the relaxed sample, the data suggest a rotation of domains and an orientation of the bundles perpendicular with the stress direction. A second stretching at an extension ratio of 2.3 has not the same effect as that performed on the original material.

Another indirect evidence of chain orientation induced by tube alignment has been obtained by infrared analysis of stretched MWNT-filled natural rubber. Natural rubber is able to crystallize under strain, a phenomenon that can be followed by infrared spectroscopy where it is seen that the band associated with the C–H out-of-plane vibration, located at  $837\text{ cm}^{-1}$  in the isotropic state shifts to higher wavenumbers upon crystallization (Fig. 8a). The change in wavenumber upon uniaxial stretching is observed at a lower extension ratio for the composite thus showing that the strain-induced crystallization process occurs at a lower deformation in the presence of carbon nanotubes as a result of a stronger orientation of polymer chains induced by alignment of filler bundles (Fig. 8b). This

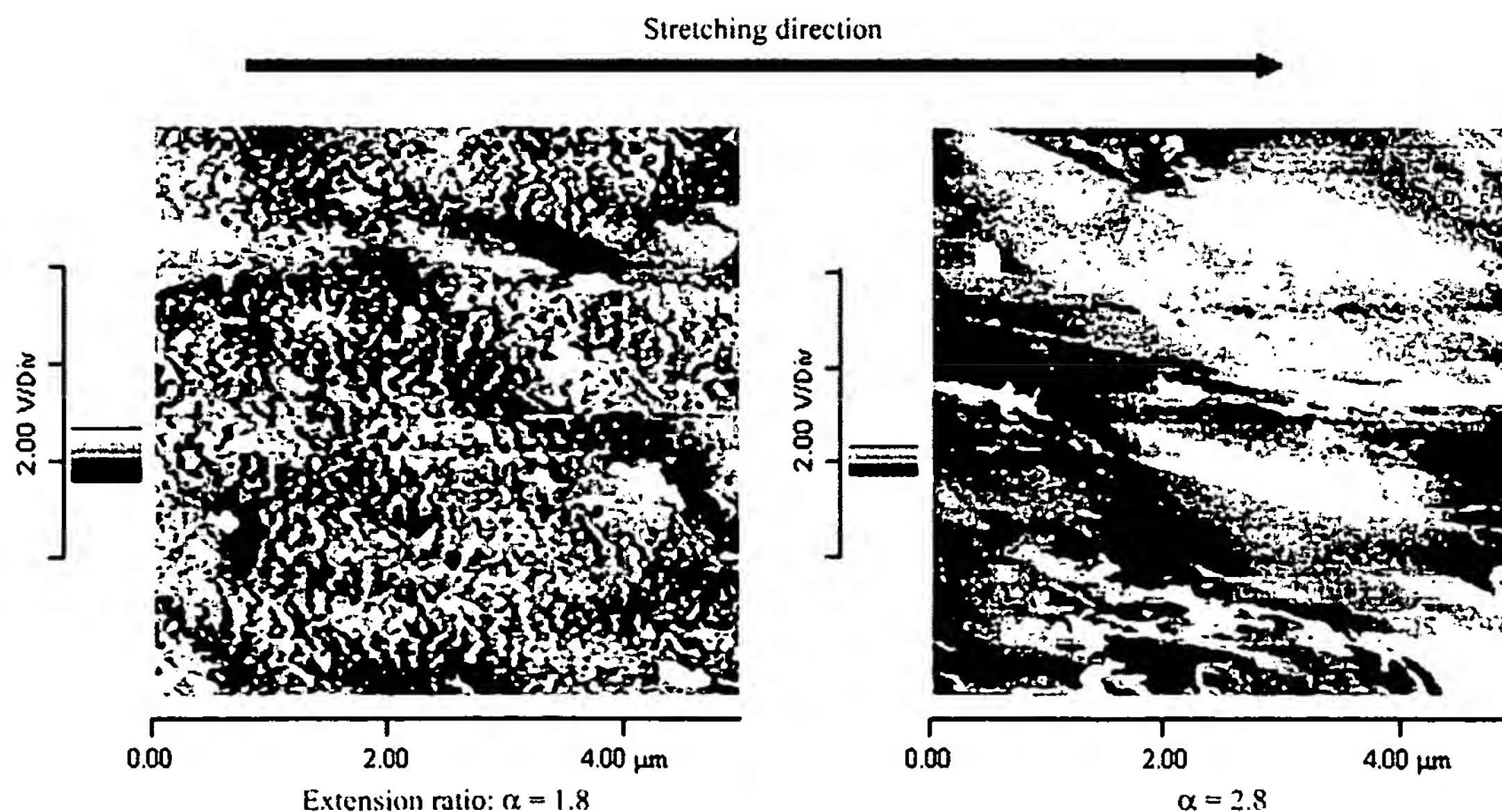


Fig. 6. Tapping-mode AFM phase-contrast images ( $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ ) for the 10 phr MWNT-filled SBR under two different elongations.



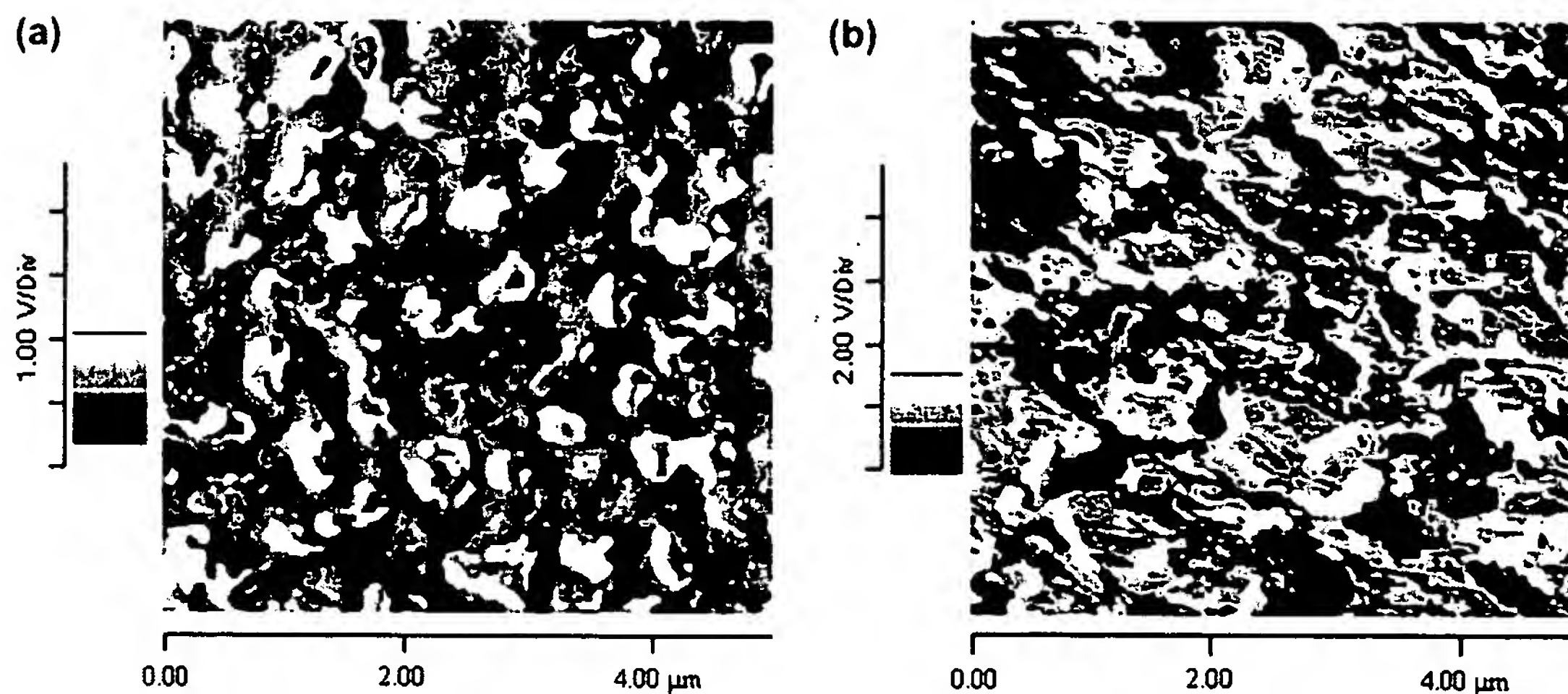


Fig. 7. AFM images after total release of the stress (a) and subsequent stretching at  $\alpha = 2.3$  (b).

interpretation which is speculative needs to be confirmed by further investigations on stretched systems.

### 5. Experimental evaluation of the interactions between carbon nanotubes and elastomers

Most of the theoretical models predicting the elastic modulus of filled rubbers assume uniform dispersion and perfect adhesion between the polymer and the matrix. TEM analysis of the composites has revealed a poor dispersion. On the other hand, the existence of interfacial interactions between the nanotubes and the matrix, which is critical in mechanical reinforcement, is not obvious. The strong restriction in equilibrium swelling in toluene with the MWNT content (Table 1) would suggest that a certain polymer–filler bonding or a state of adhesion between the two phases is established. But a more realistic interpretation of the swelling deficit in the presence of carbon nanotubes would be the occlusion of rubber into the aggregates. During processing, carbon nanotubes are well dispersed in toluene solution and then reaggregate after

incorporation of polymer thus entrapping elastomer molecules which behave like filler and do not swell [105]. On the other hand, some hysteresis (area between the first stretch and the second stretch) has been observed at large strains for the samples filled with MWNTs (Fig. 9). After stretching and release, the sample exhibits a large degree of permanent deformation. The hysteresis, also called “stress-softening effect” has been shown to correspond, in the case of conventional composites, to a loss of elastic chains taking place at the polymer–filler interface [86]. It is very low in the case of poor polymer–filler interactions [106]. In view of the AFM observations, we are in a position to believe that in carbon nanotube-filled samples, the stress–strain behavior of the composites contains a large contribution arising from orientational effects and that the pronounced lowering in the stress observed in the second stretching corresponds to a loss of orientation once the stress is released.

Dynamic mechanical analysis measurements were performed on pure natural rubber (NR) and composites with up to 10 phr of MWNTs. The temperature dependence of the

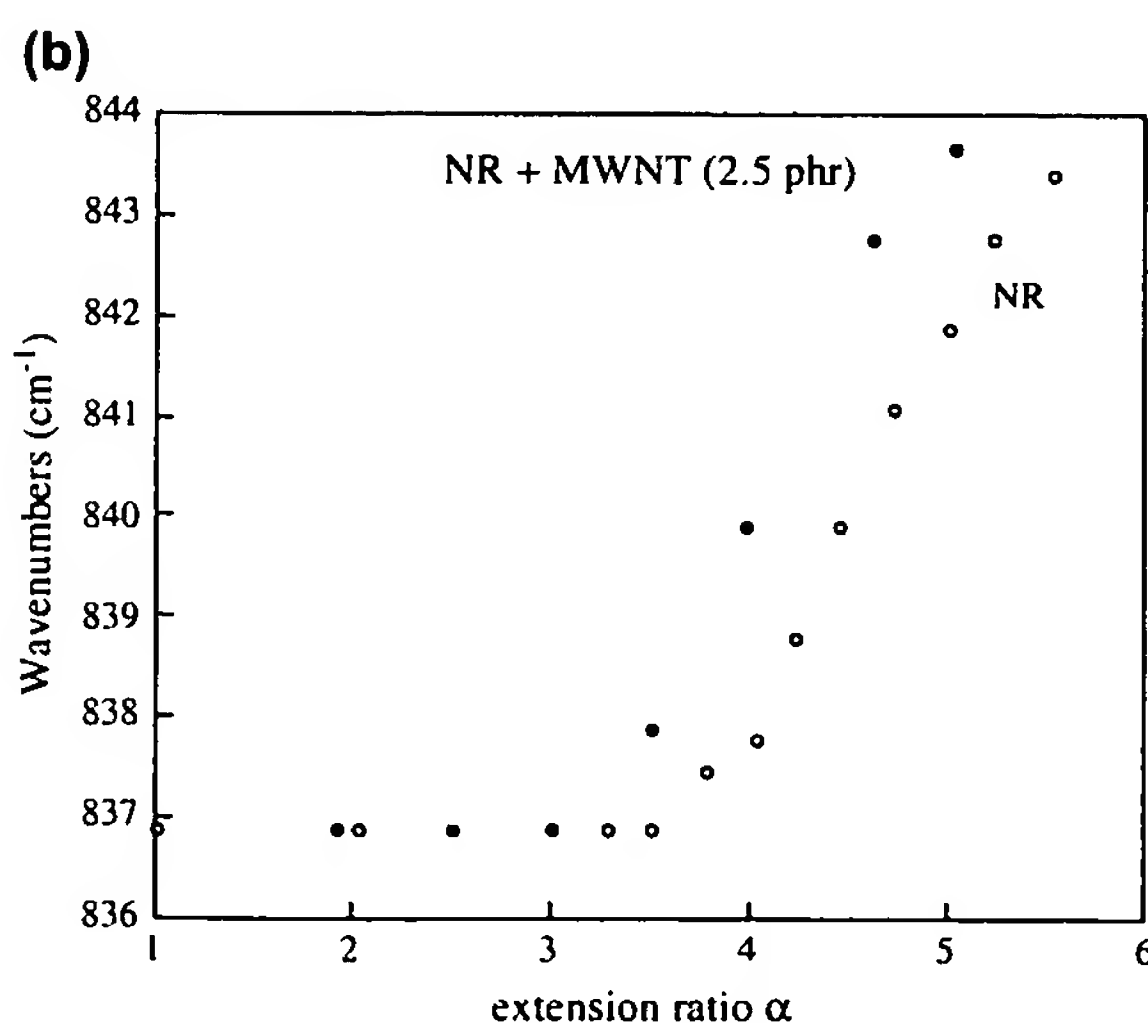
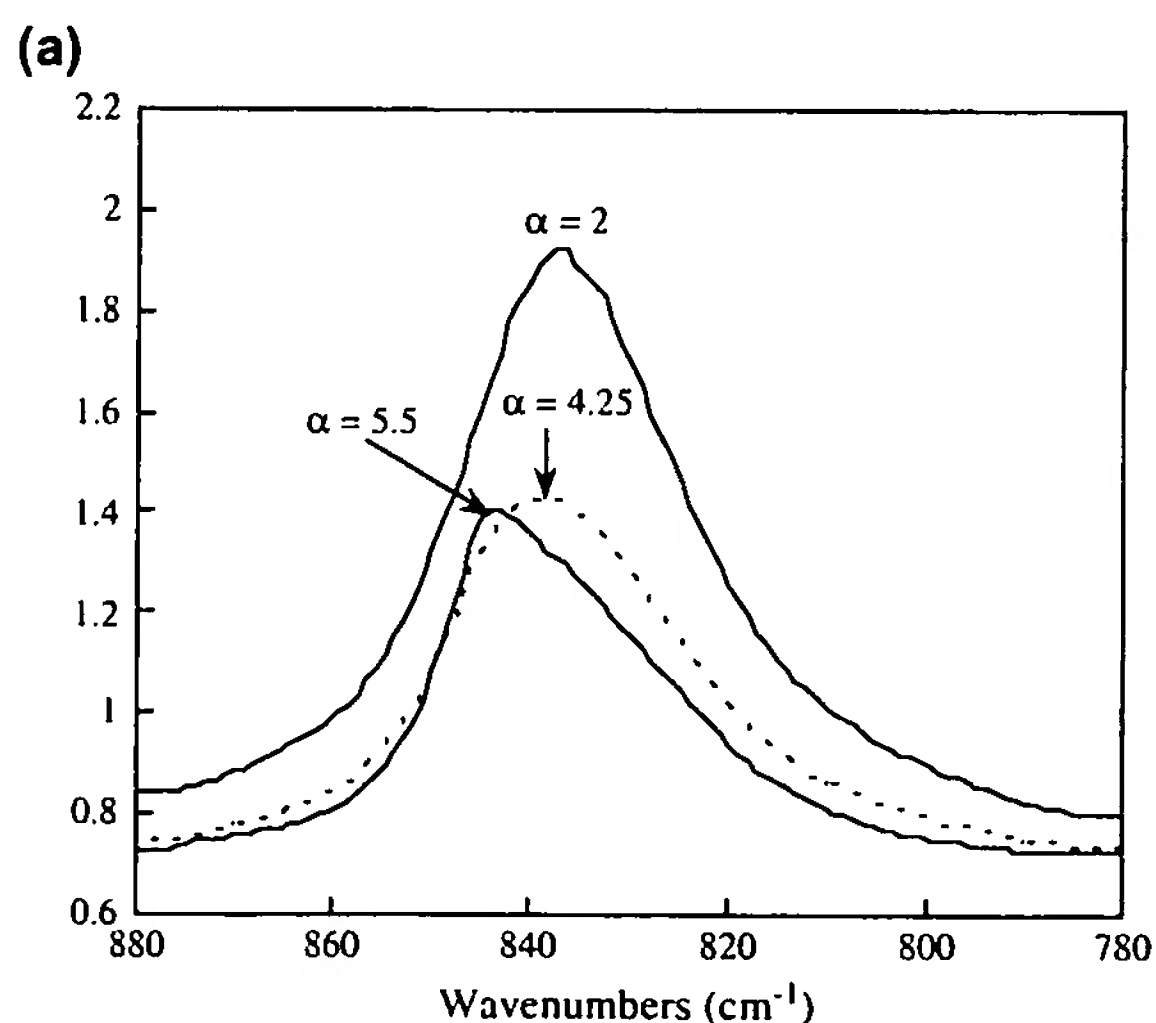


Fig. 8. Shift of the C–H out-of-plane absorption band upon crystallization of unfilled natural rubber (a) and dependence of its wavenumber on the extension ratio  $\alpha$  (b).

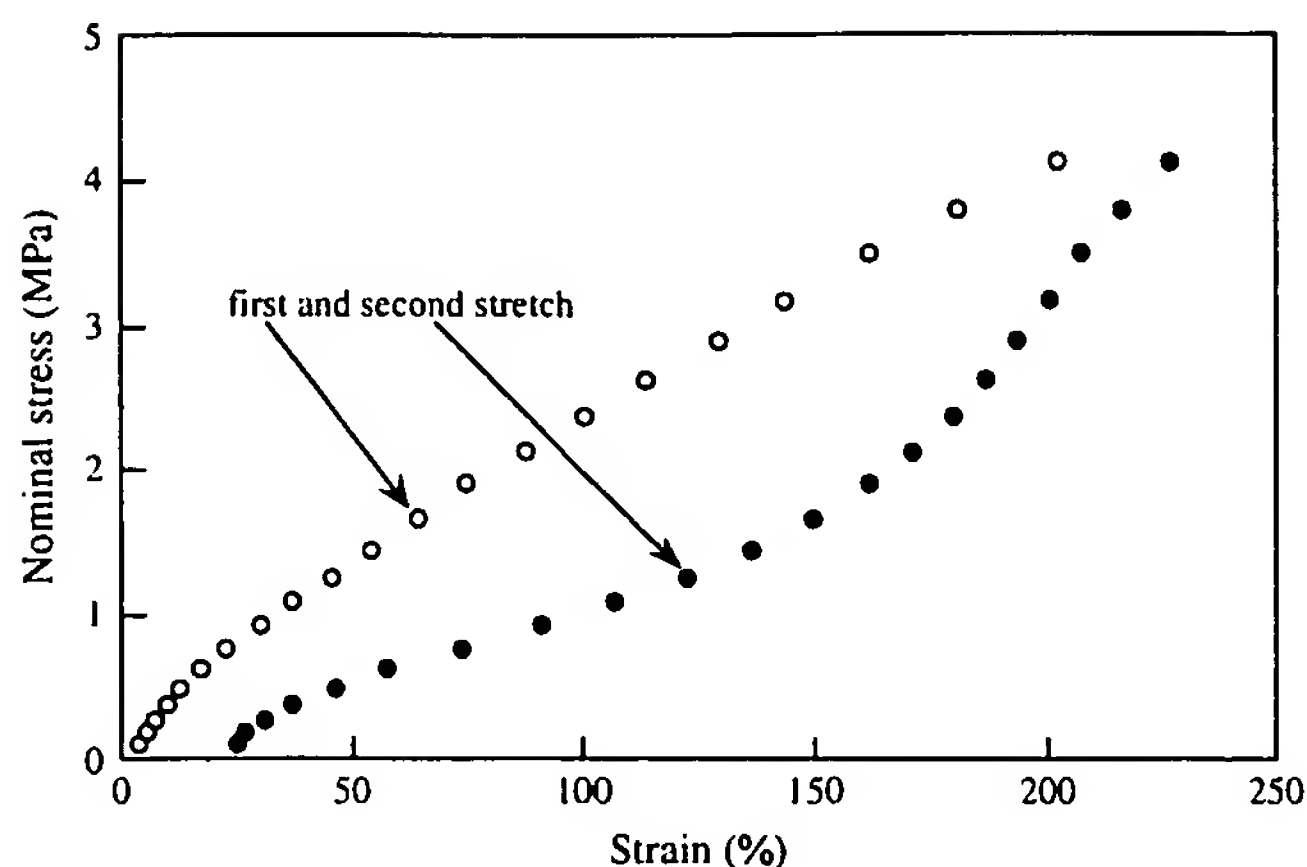


Fig. 9. Mullins hysteresis for the SBR/10 phr MWNT composite.

storage modulus  $G'$  and of the loss factor  $\tan \delta$  for the unfilled and 10 phr MWNT-filled NR are reported in Fig. 10. Around  $-60^\circ\text{C}$ , the storage modulus  $G'$  decreases abruptly while  $\tan \delta$  passes through a maximum. This relaxation process is of course related to an energy dissipation associated with the glass transition phenomenon of the rubber phase. As seen in Fig. 10, the glass transition temperature taken at the maximum of  $\tan \delta$  does not change significantly upon incorporation of the nanotubes in the matrix, since the  $T_g$  values increases from  $-61.3^\circ\text{C}$  for pristine NR to  $-59.8^\circ\text{C}$  for the filled sample. This small effect of MWNTs on the glass transition temperature of the rubber cannot be a sign of a lack of adhesion of the filler to the elastomer since several authors have reported little influence of the presence of carbon blacks on  $T_g$  even at high filler loading and with reinforcing blacks [82].

In conventional composites, the adsorption of polymer molecules gives rise to the formation of an adsorption layer, evidenced by dielectric or solid state NMR spectroscopies [5,107], whose thickness has been estimated around 2 or 3 nm and where motions of chain units are more restricted than those in the mobile phase. The loss in segmental mobility would result in an increase in  $T_g$  and most probably in a change of the thermal expansion of the free volume. Surprisingly, investigations carried out on a styrene–butadiene copolymer

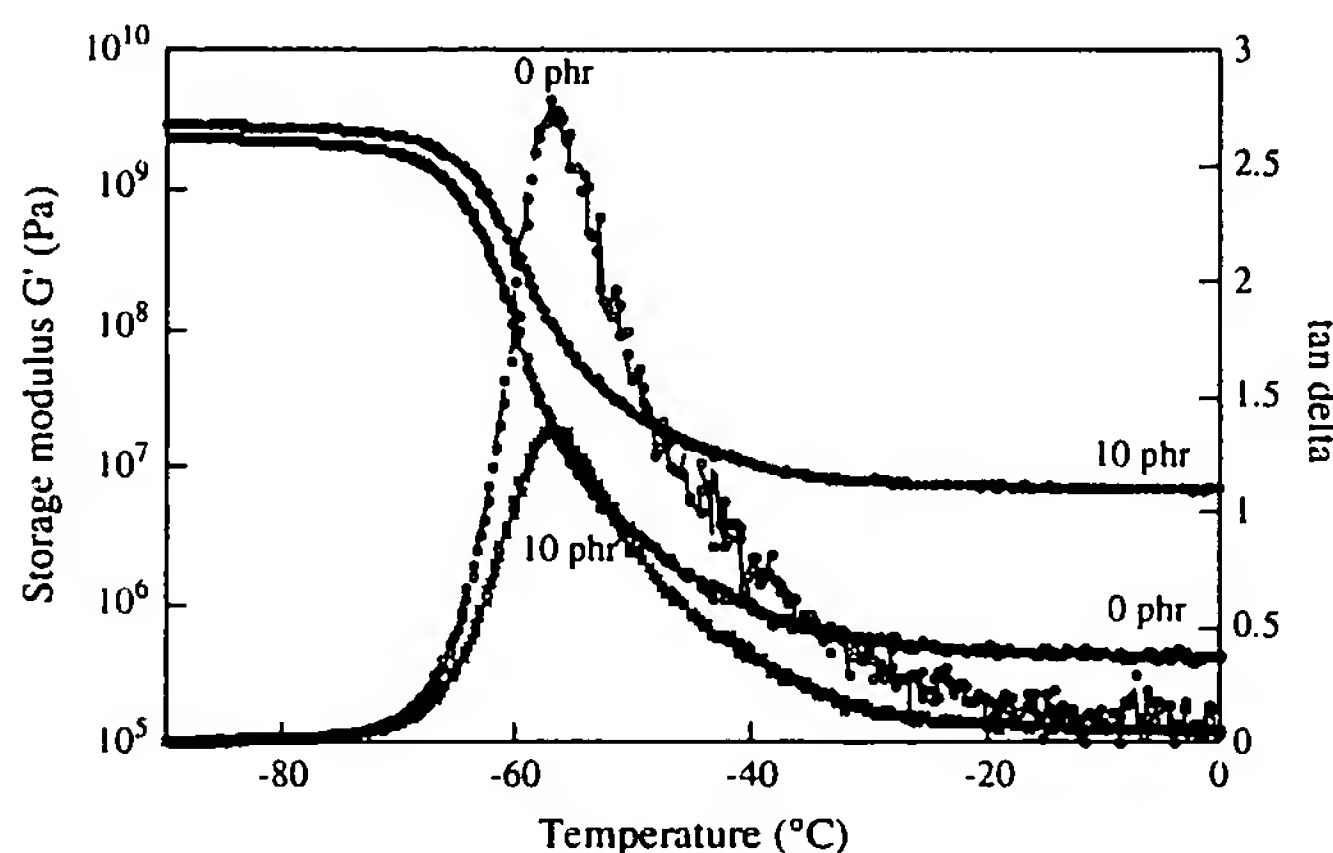


Fig. 10. Temperature dependence of the storage modulus and of the loss factor for pure NR and NR/10 phr MWNT composite.

filled with different carbon blacks, show that  $T_g$  is only increased by about  $1^\circ\text{C}$  by every 50 phr of highly reinforcing filler but remains unaffected by relatively inert carbon black while the coefficient of expansion of the polymer component of the composite is substantially unaffected by all carbon blacks in the rubbery region [108].

For composites of poly(methyl methacrylate (PMMA) and unmodified SWNTs  $\tan \delta$  peak broadens but the peak is at the  $105^\circ\text{C}$  value of bulk polymer for the unfunctionalized composite while the amide-functionalized PMMA composite displays a  $\tan \delta$  peak shifted to a higher temperature by  $30^\circ\text{C}$  with regard to the pure polymer [56]. The amide-functionalized PMMA composite displays a  $\tan \delta$  peak shifted to a higher temperature by  $30^\circ\text{C}$  with regard to the pure polymer. The authors suggest the existence of discrete interphase regions with unmodified SWNTs due to clustering of tubes while the functionalized composite system has a stronger interfacial bonding via the covalent linkages between the two phases leading to the formation of an extensive region with altered properties. From SEM analysis of MWNT/polycarbonate composites, Pötschke et al. [109] and Ding et al. [110] observed tube diameters larger than those of the pristine MWNTs used in the sample preparation and suggest the existence of an adsorbed layer of polymer on the tubes' surface but unfortunately do not mention if a shift in  $T_g$  is associated with the tube coating. Additionally, a dependence of the nanotube content on the glass transition temperature was observed for MWNT/epoxy composites with a stronger increase in  $T_g$  for samples containing amino-functionalized nanotubes [55]. The authors do not exclude a possible effect of the additional functional groups on the curing reaction of the epoxy matrix.

As seen in Fig. 10, at higher temperatures, the storage modulus reaches a plateau around 0.3 MPa at  $20^\circ\text{C}$  for the unfilled NR and 6.2 MPa for the composite. This large modulus increase in the rubbery plateau, which represents the reinforcement provided by the carbon nanotubes, is much higher than that obtained in the tensile mechanical characterization because it includes the contribution arising from filler–filler interactions. This contribution is usually evidenced through the strain dependence of the storage modulus. Reinforced elastomers and more generally systems containing filler dispersions are characterized by a non-linear viscoelastic behavior, known as the “Payne effect” [111,112]. With regard to the unfilled rubber, the composite containing 10 phr of MWNTs has been shown to display a greater Payne effect probably associated with the breakdown of large agglomerates of carbon nanotubes (Fig. 11).

Interactions between the nanotube bundles and the matrix are required for an efficient stress transfer from the matrix to the nanotubes. Raman spectroscopy has proved to be very sensitive for an evaluation of the strength of the polymer–filler interface. In fact, carbon nanotubes exhibit well-defined Raman peaks located for our MWNTs at  $1345$ ,  $1595$  and  $2700\text{ cm}^{-1}$ , respectively, assigned to the disordered graphite structure (D band), tangential stretching mode of carbon–carbon bonds (G band) and to the overtone of the D band ( $G'$  band) (Fig. 12). Cooper et al. [113] have shown that the  $G'$  band shifts to a lower wavenumber upon application of a tensile stress on

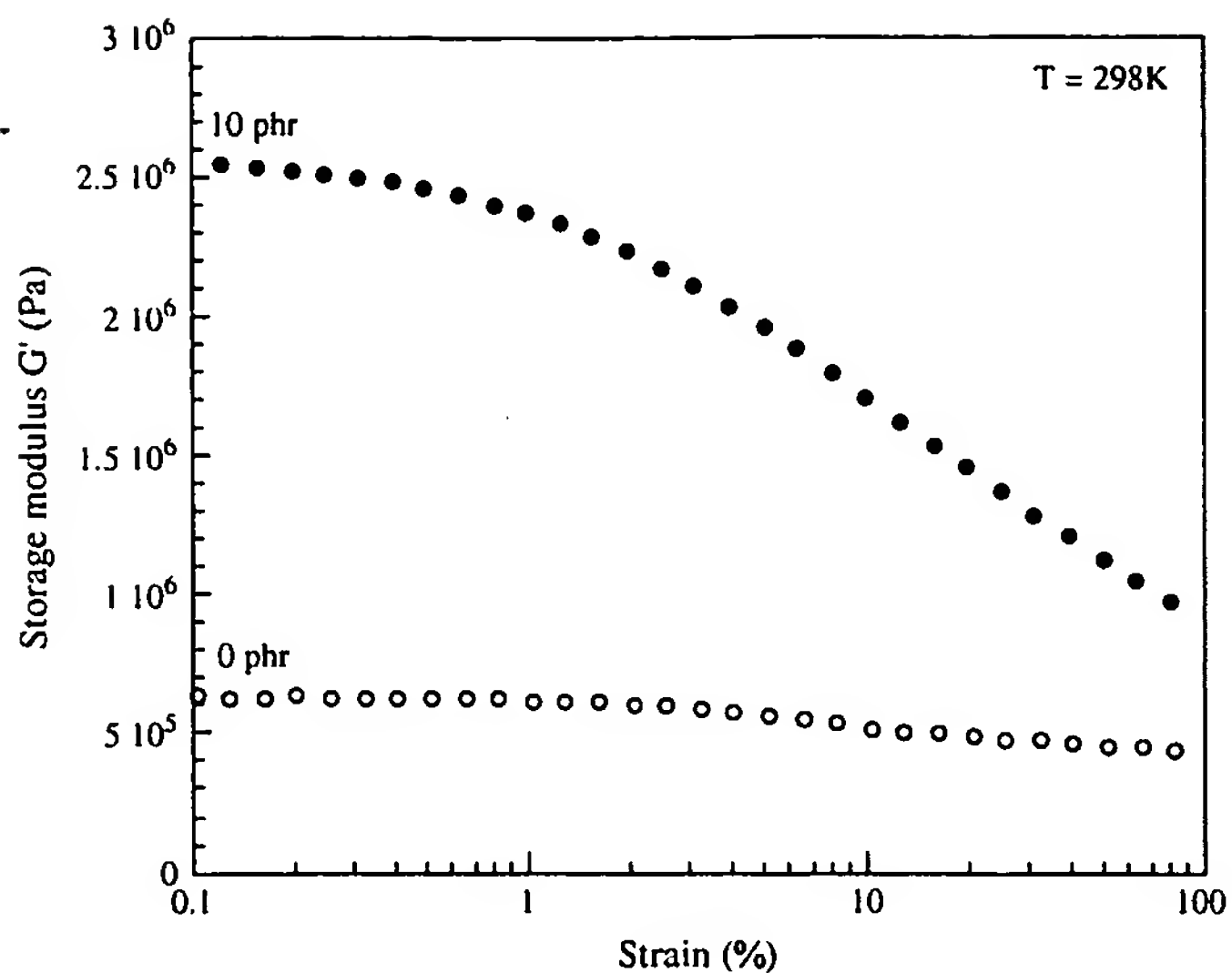


Fig. 11. Strain dependence of the storage modulus for pure NR and NR/10 phr MWNT composite.

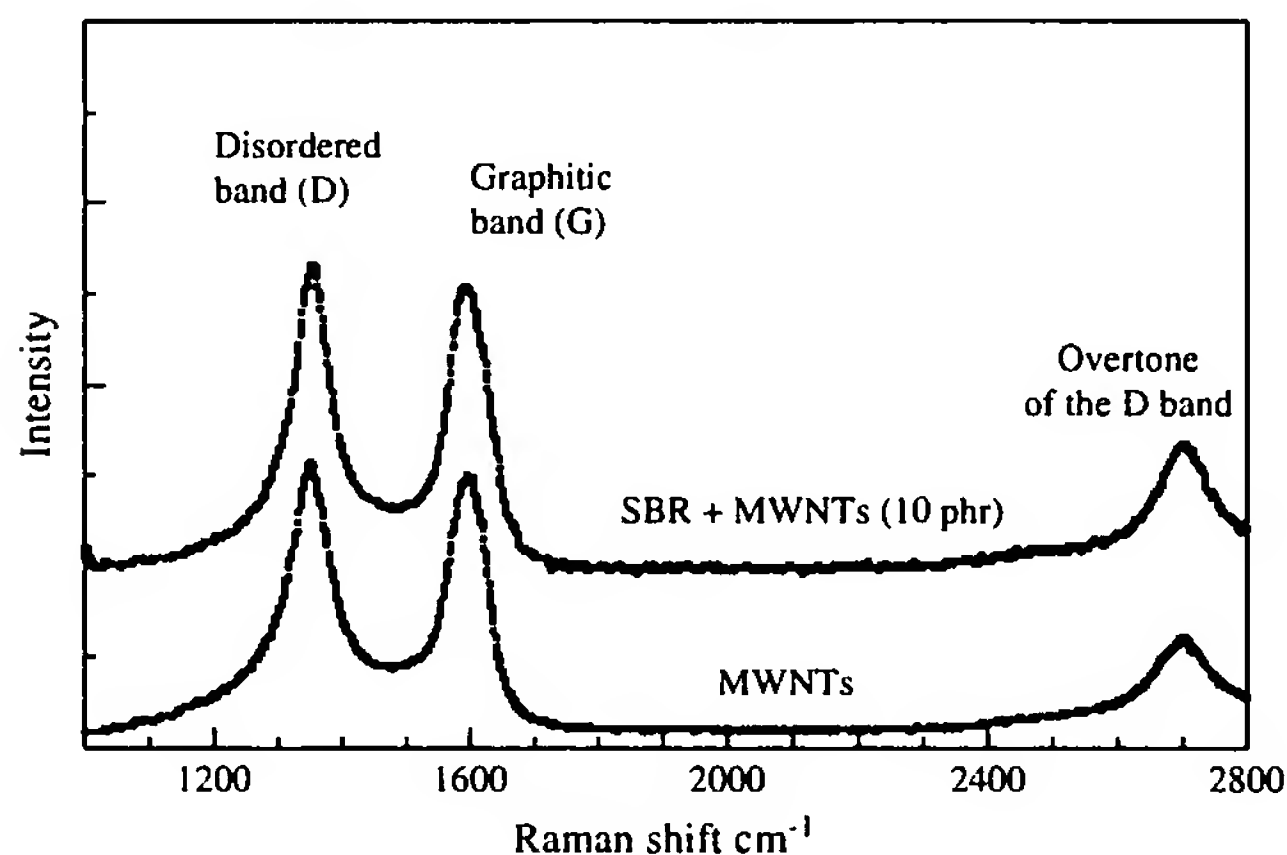


Fig. 12. Raman spectra of pure MWNTs and SBR/MWNT composite at 514 nm excitation. Intensities of the spectra have been adjusted to improve presentation.

composites based on epoxy resins and single or multiwall carbon nanotubes. According to the authors, this shift indicates stress transfer from the matrix to the nanotubes and hence reinforcement. Nevertheless, the rates of band shift were found to differ for all the nanotubes investigated. Poorer dispersion, worse adhesion and lower aspect ratio were invoked to account for smaller shift rate. In our case, the Raman peaks were not found to shift when the composite is subjected to an extensional strain, indicating weak interfacial interactions.

## 6. Electrical properties

In addition to improving the mechanical properties, black fillers (carbon black or carbon nanotubes) impart conductivity to low resistivity elastomeric matrices. In many applications, electrical conductivity is required to dissipate electrostatic charge. The electrical properties are strongly affected by the filler concentration, the filler morphology such as particle size and structure as well as filler–filler and filler–matrix interactions which determine the state of dispersion. Nanotube orientation will also influence the electrical conductivity. There is a critical volume fraction known as the percolation threshold at which the conducting inclusions form an interconnecting filler network leading to a sharp drop in the electrical resistance.

Fig. 13 shows the effect of filler loading on the volume resistivity of carbon black (N330 from Cabot) (CB) and MWNT-filled composites based on insulating styrene–butadiene rubber. Electrical resistivity measurements were determined on samples of  $10 \times 20 \times 0.2 \text{ mm}^3$  by measuring their resistance on a high resistance meter (Keithley 6517A) between two conductive rubber electrodes with an alternative voltage of 1 V. This alternative voltage is needed to avoid a background current effect. The measured resistances  $R$  were then converted into volume resistivity  $\rho$  using the following equation:

$$\rho = \frac{RS}{d} \quad (5)$$

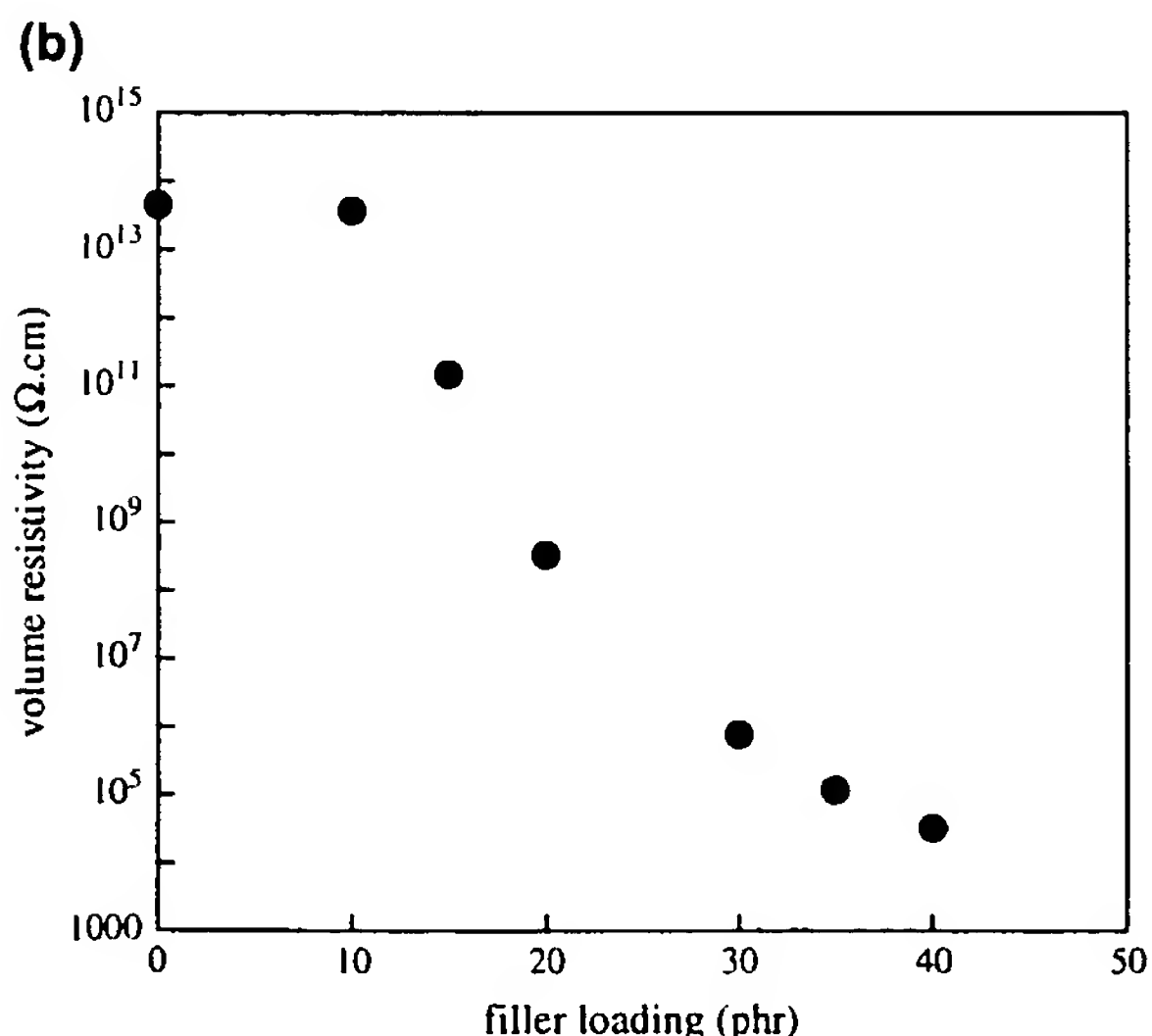
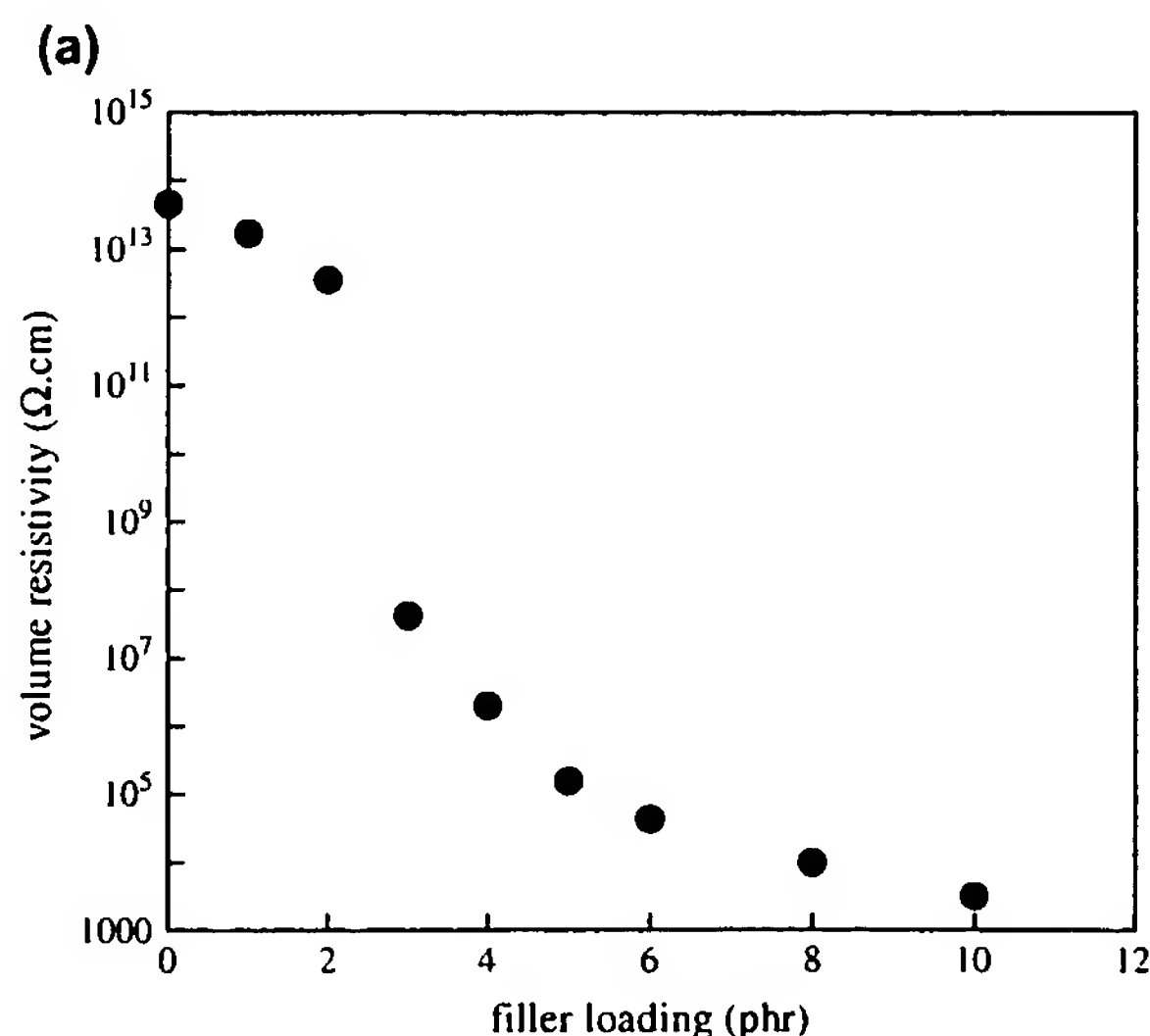


Fig. 13. Volume resistivity against filler loading for SBR composites filled with MWNTs (a) or CB (b).



where  $S$  is the cross-sectional area perpendicular to the current and  $d$  is the thickness of the sample between the two electrodes.

The continuous network is formed at a lower filler loading of the nanotube bundles with MWNTs than with CB. The higher aspect ratio of the nanotube bundles which increases the probability of particle–particle contacts explain the low percolation threshold. Our results are in agreement with those of Flandin et al. [114] and of Thongruang et al. [115] who showed that the percolation-threshold concentration in composites is around 10–15 wt.% for carbon fiber and high structure carbon black and around 40–50 wt.% for low structure carbon black and graphite. The high electrical conductivity of carbon nanotube-filled composites obtained at a relatively low volume fraction is one of the major attributes of carbon nanotubes since that allows to retain the desired mechanical properties. The higher loadings of carbon black, required to provide the same level of conductivity, often lead to an increase in viscosity and consequently to a reduction and processing ease and can be associated with a reduction in mechanical properties.

Since the resistivity of the unfilled elastomer is several orders of magnitude larger than that of the filled vulcanizate, any rearrangement of the filler particle distribution induced, for example, by application of a deformation, leads to a change in the vulcanizate conductivity. Significant changes in electrical resistivity against deformation in black-filled composites have already been reported in the literature [114,116–121]. At small deformations, changes in dynamic moduli with strain amplitude have been found to be very similar to changes in conductivity with strain amplitude [116–118]. The storage modulus,  $G'$  and the dynamic conductivity have been shown to decrease in a similar way as the amplitude of dynamic oscillation was increased. The reduction of both conductivity and modulus has been associated with the breakdown of the carbon network.

Here, is considered, the effect of a uniaxial deformation on the electrical properties of a material whose MWNT concentration is above the insulator–conductor transition region. To measure changes in resistivity, strips (size:  $50 \times 15 \times 1 \text{ mm}^3$ ) were stretched with a manual stretching machine in which two clamps connected to the high resistance meter, were placed along the length of the specimen (Fig. 14).

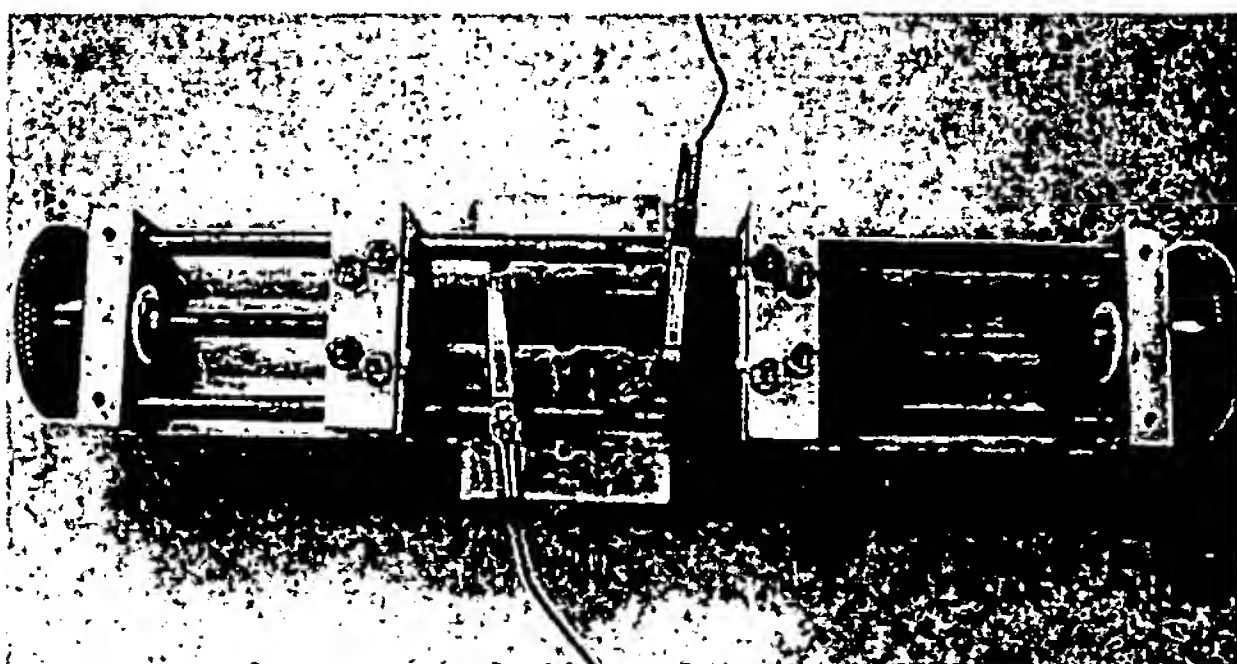


Fig. 14. Stretching machine for electrical measurements under uniaxial extension.

Measurements were made at about 5 mn after each elongation step. Static resistance,  $R$ , of the vulcanizate under uniaxial extension was measured in the direction of strain and the resistivity,  $\rho$ , was calculated from the following expression:

$$\rho = \frac{RS}{L} = \frac{RS_0}{\alpha^2 L_0} \quad (6)$$

where  $S_0$  and  $L_0$  are, respectively, the initial cross-sectional area and length between the two clamps before deformation and  $\alpha$  is the extension ratio. Under uniaxial extension, the deformed length,  $L$ , becomes  $\alpha L_0$  while  $S$  is equal to  $S_0/\alpha$ , if the volume remains constant during deformation.

The change in resistivity during uniaxial extension for a composite filled with 10 phr of MWNTs is shown in Fig. 15. It is observed that the resistivity of the sample increases gradually with the applied strain. Our results differ from those presented by Yamaguchi et al. [121] for carbon black-filled elastomers where an increase in resistivity at low strains is observed, followed by a subsequent reduction at higher extensions. The authors explain the rise in the initial resistivity by a breakdown of carbon black agglomerates into smaller aggregates and consequently a reduction in the total number of conduction paths. They attribute the subsequent reduction to the orientation of the carbon black aggregates in the direction of strain. Das et al. [120] observed, for carbon black and short carbon fiber filled rubber composites, that the resistivity increases rapidly with the degree of elongation strain and explain the increase in resistivity by a breakdown of existing conductive networks and formation of new conductive networks by rearrangements and orientation of black particle aggregates or fibers. Donnet and Voet [118] consider that the strain dependence of the electrical properties of carbon black-loaded vulcanizates can be interpreted at small extensions by the reversible formation and destruction of the transient carbon network, up to 150% extension by an orientation of carbon

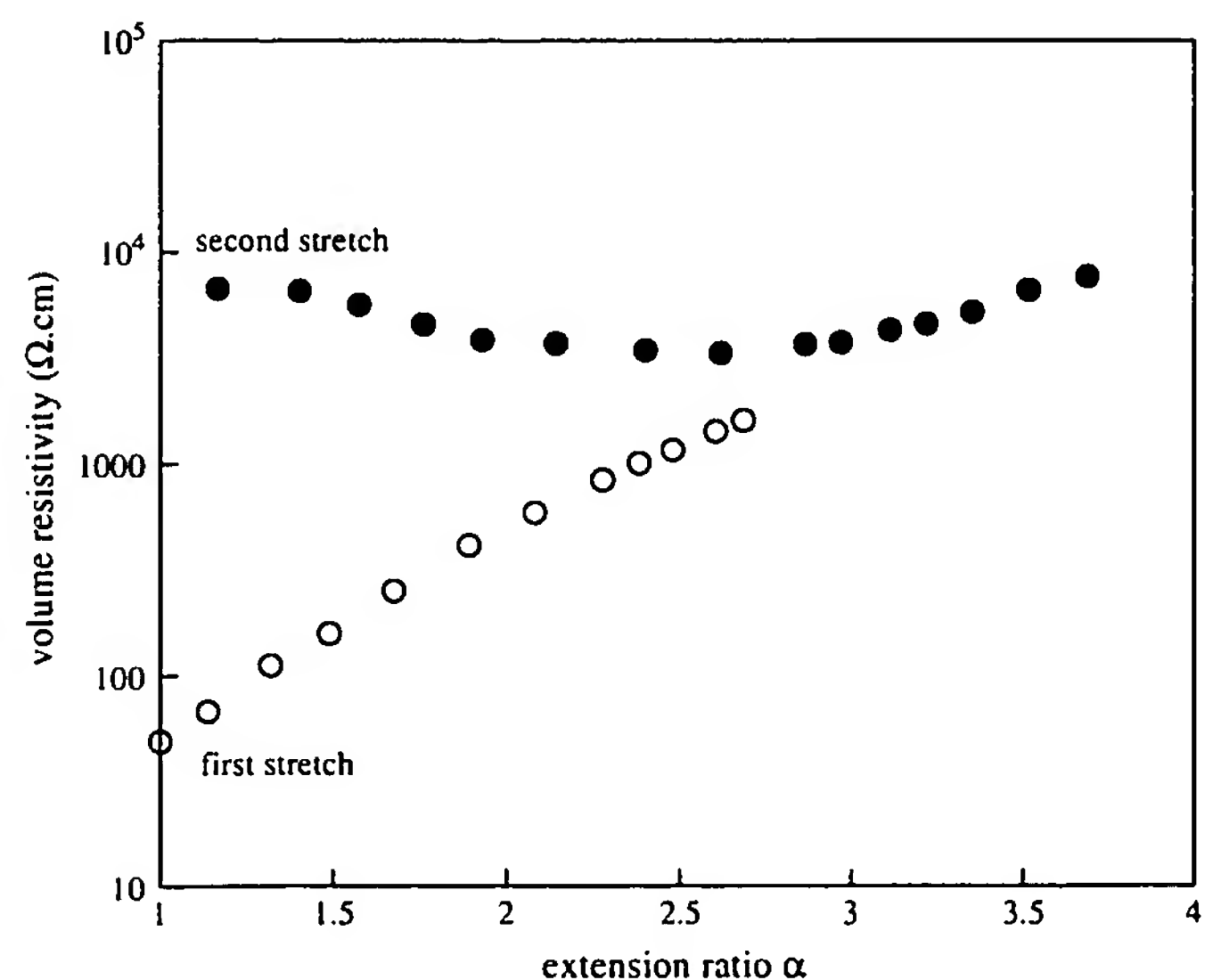


Fig. 15. Dependence of the electrical resistivity on the extension ratio  $\alpha$  for the SBR/10 phr MWNT composite.

black aggregates and to rupture of elastomer–carbon bonds at still higher extensions.

According to our AFM experiments under strain, we ascribe the gradual increase in resistivity with strain (Fig. 15) to the orientation of the nanotube bundles rather than to the destruction of large filler structures. Our interpretation is in agreement with the results of Du et al. [48] who showed that alignment of a nanotubes worsens the electrical conductivity and also shifts the percolation threshold.

In order to parallel the mechanical measurements, electrical measurements are also carried out during a second stretching performed 1 h after total unloading of the sample.

After total unloading of the sample, as already reported in other studies [120,121], the resistivity of the fully relaxed composite is significantly higher than that measured in the unstrained elastomer showing that the filler network is not re-formed after removal of the stress. During the second stretching performed 1 h after retraction, the resistivity slightly decreases on account of a reformation of new conductive contacts. When the strain reaches the maximum value of the first stretching, the two curves coincide which means that the sample is in the same state as it was at the first stretching. In light of the AFM experimental observations, we can ascribe the strong hysteresis in the conductivity–strain curve to rearrangements and disorientation of the bundles.

## 7. Conclusion

In this review, results obtained on carbon nanotube reinforced polymers are presented. While the polymeric media are focused on elastomeric matrices, results obtained on other materials are also mentioned when needed in the discussion.

After a brief presentation on the synthesis methods and processing of nanotube-based polymer composites, the factors expected to control their mechanical properties are discussed in relation to what is already known on composites filled with conventional fillers such as carbon black or silica. Specific features of carbon nanotubes related to their modulus, geometry and orientation, are also taken into account. In particular, atomic force microscopy imaging under uniaxial extension of the sample gives evidence of the contribution of the orientational effects.

Poor dispersion and lack of interfacial adhesion between the tubes and the polymer are limiting factors for full realization of filler capability. Up to now, the improvements in mechanical properties of the neat polymer by carbon nanotube incorporation remain modest with regard to what should be expected from a nanometer-scale reinforcement. This demonstrates the need for optimizing the processing conditions to achieve good dispersion and good interactions with the polymer chains. This could be done by an appropriate functionalization of the tube surface or by introducing in the medium a type of coupling agent able to react with both phases. On the other hand, a method of incorporating simultaneously carbon nanotubes and another type of filler, namely carbon black particles, could be of interest on account of possible synergistic effects that could arise between the two different fillers.

Through a combination of benefits of each type of filler, these hybrid composites could potentially exhibit improved characteristics with regard to single-filler materials. In particular, carbon black particles may improve the formation of connected structures by bridging uncontacted tubes.

The capability of carbon nanotubes to impart conductivity to insulating elastomeric matrices has been clearly shown. Electrical measurements carried out under uniaxial deformation display a gradual increase in resistivity as a result of a breakdown and an orientation of the filler particles.

In conclusion, this preliminary experimental work in carbon nanotube-based elastomeric composites has demonstrated the potential of this new form of carbon as a reinforcing filler of rubber materials. Most markedly, this work has illustrated the problems encountered with the dispersion and interaction in the host polymeric medium.

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# Advances in the science and technology of carbon nanotubes and their composites: a review

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## Abstract

Since their first observation nearly a decade ago by Iijima (Iijima S. Helical microtubules of graphitic carbon *Nature*. 1991; 354:56–8), carbon nanotubes have been the focus of considerable research. Numerous investigators have since reported remarkable physical and mechanical properties for this new form of carbon. From unique electronic properties and a thermal conductivity higher than diamond to mechanical properties where the stiffness, strength and resilience exceeds any current material, carbon nanotubes offer tremendous opportunities for the development of fundamentally new material systems. In particular, the exceptional mechanical properties of carbon nanotubes, combined with their low density, offer scope for the development of nanotube-reinforced composite materials. The potential for nanocomposites reinforced with carbon tubes having extraordinary specific stiffness and strength represent tremendous opportunity for application in the 21st century. This paper provides a concise review of recent advances in carbon nanotubes and their composites. We examine the research work reported in the literature on the structure and processing of carbon nanotubes, as well as characterization and property modeling of carbon nanotubes and their composites. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

In the mid 1980s, Smalley and co-workers at Rice University developed the chemistry of fullerenes [2]. Fullerenes are geometric cage-like structures of carbon atoms that are composed of hexagonal and pentagonal faces. The first closed, convex structure formed was the C<sub>60</sub> molecule. Named after the architect known for designing geodesic domes, R. Buckminster Fuller, buckminsterfullerene is a closed cage of 60 carbon atoms where each side of a pentagon is the adjacent side of a hexagon similar to a soccer ball (the C<sub>60</sub> molecule is often referred to as a bucky ball) [2]. A few years later, their discovery led to the synthesis of carbon nanotubes. Nanotubes are long, slender fullerenes where the walls of the tubes are hexagonal carbon (graphite structure) and often capped at each end.

These cage-like forms of carbon have been shown to exhibit exceptional material properties that are a

consequence of their symmetric structure. Many researchers have reported mechanical properties of carbon nanotubes that exceed those of any previously existing materials. Although there are varying reports in the literature on the exact properties of carbon nanotubes, theoretical and experimental results have shown extremely high elastic modulus, greater than 1 TPa (the elastic modulus of diamond is 1.2 TPa) and reported strengths 10–100 times higher than the strongest steel at a fraction of the weight. Indeed, if the reported mechanical properties are accurate, carbon nanotubes may result in an entire new class of advanced materials. To unlock the potential of carbon nanotubes for application in polymer nanocomposites, one must fully understand the elastic and fracture properties of carbon nanotubes as well as the interactions at the nanotube/matrix interface. Although this requirement is no different from that for conventional fiber-reinforced composites [3], the scale of the reinforcement phase diameter has changed from micrometers (e.g. glass and carbon fibers) to nanometers.

In addition to the exceptional mechanical properties associated with carbon nanotubes, they also possess

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superior thermal and electric properties: thermally stable up to 2800 °C in vacuum, thermal conductivity about twice as high as diamond, electric-current-carrying capacity 1000 times higher than copper wires [4]. These exceptional properties of carbon nanotubes have been investigated for devices such as field-emission displays [5], scanning probe microscopy tips [6], and micro-electronic devices [7,8]. In this paper we provide an overview of the recent advances in processing, characterization, and modeling of carbon nanotubes and their composites. This review is not intended to be comprehensive, as our focus is on exploiting the exceptional mechanical properties of carbon nanotubes toward the development of macroscopic structural materials. Indeed, the exceptional physical properties of carbon nanotubes also present the opportunity to develop multifunctional nanotube composites with tailored physical and mechanical properties.

## 2. Atomic structure and morphology of carbon nanotubes

Carbon nanotubes can be visualized as a sheet of graphite that has been rolled into a tube. Unlike diamond, where a 3-D diamond cubic crystal structure is formed with each carbon atom having four nearest neighbors arranged in a tetrahedron, graphite is formed as a 2-D sheet of carbon atoms arranged in a hexagonal array. In this case, each carbon atom has three nearest neighbors. 'Rolling' sheets of graphite into cylinders forms carbon nanotubes. The properties of nanotubes depend on atomic arrangement (how the sheets of graphite are 'rolled'), the diameter and length of the tubes, and the morphology, or nano structure. Nanotubes exist as either single-walled or multi-walled structures, and multi-walled carbon nanotubes (MWCNTs) are simply composed of concentric single-walled carbon nanotubes (SWCNTs).

### 2.1. Nanotube structure

The atomic structure of nanotubes is described in terms of the tube chirality, or helicity, which is defined by the chiral vector,  $\vec{C}_h$ , and the chiral angle,  $\theta$ . In Fig. 1, we can visualize cutting the graphite sheet along the dotted lines and rolling the tube so that the tip of the chiral vector touches its tail. The chiral vector, often known as the roll-up vector, can be described by the following equation:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \quad (1)$$

where the integers ( $n, m$ ) are the number of steps along the zig-zag carbon bonds of the hexagonal lattice and  $\vec{a}_1$  and  $\vec{a}_2$  are unit vectors, shown in Fig. 1. The chiral angle determines the amount of 'twist' in the tube. The

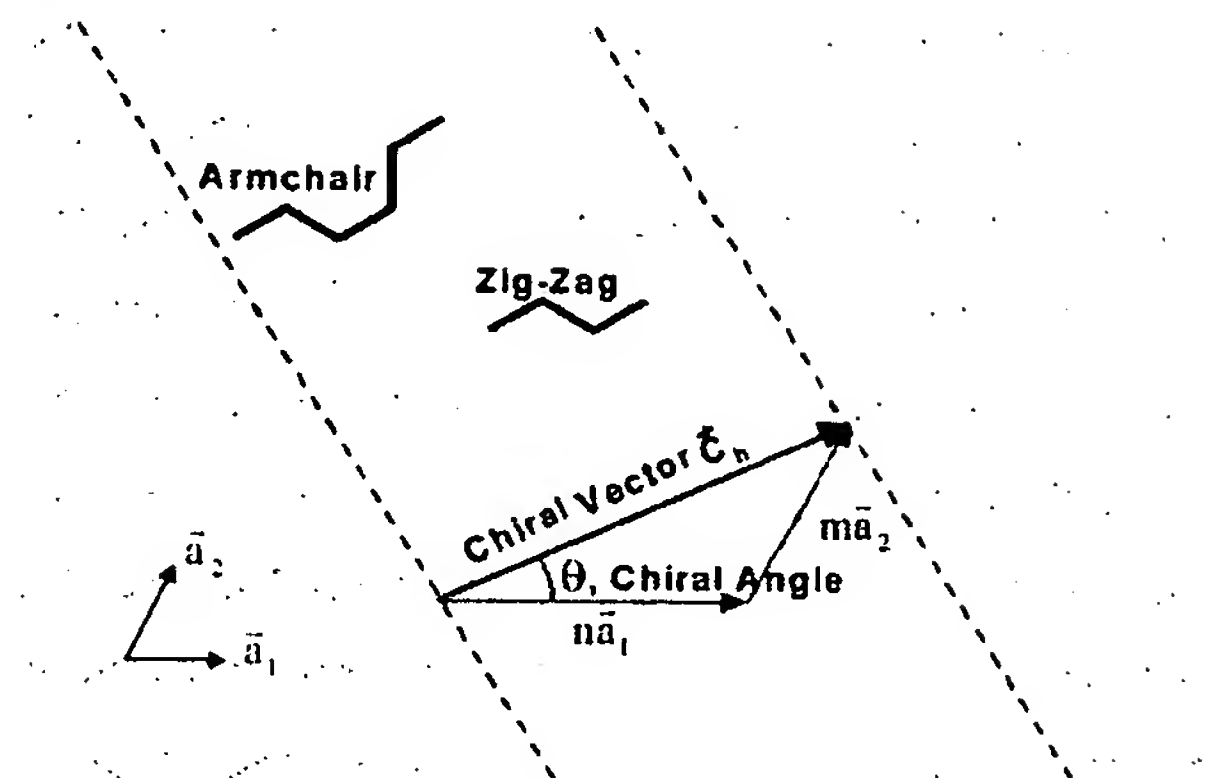


Fig. 1. Schematic diagram showing how a hexagonal sheet of graphite is 'rolled' to form a carbon nanotube.

two limiting cases exist where the chiral angle is at 0° and 30°. These limiting cases are referred to as zig-zag (0°) and armchair (30°) based on the geometry of the carbon bonds around the circumference of the nanotube. The difference in armchair and zig-zag nanotube structures is shown in Fig. 2. In terms of the roll-up vector, the zig-zag nanotube is ( $n, 0$ ) and the armchair nanotube is ( $n, n$ ). The roll-up vector of the nanotube also defines the nanotube diameter since the inter-atomic spacing of the carbon atoms is known.

The chirality of the carbon nanotube has significant implications on the material properties. In particular, tube chirality is known to have a strong impact on the electronic properties of carbon nanotubes. Graphite is considered to be a semi-metal, but it has been shown that nanotubes can be either metallic or semiconducting, depending on tube chirality [9].

Investigations on the influence of chirality on the mechanical properties have also been reported. The analytical work of Yakobson et al. [10,11] examined the

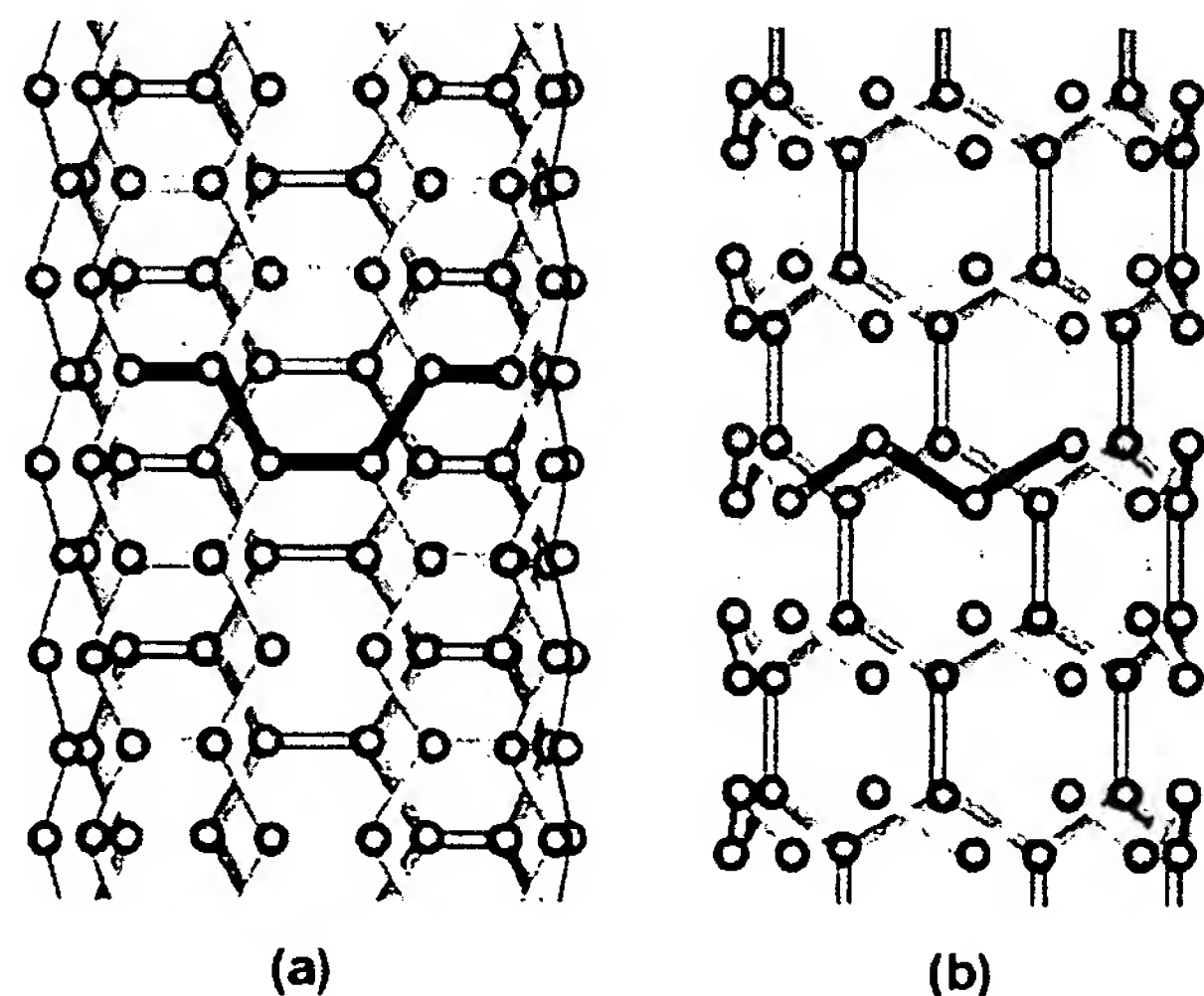


Fig. 2. Illustrations of the atomic structure of (a) an armchair and (b) a zig-zag nanotube.

instability of carbon nanotubes beyond linear response. Their simulations show that carbon nanotubes are remarkably resilient, sustaining extreme strain with no signs of brittleness or plasticity. Although the chirality has a relatively small influence on the elastic stiffness, they concluded that the Stone-Wales transformation, a reversible diatomic interchange where the resulting structure is two pentagons and two heptagons in pairs, plays a key role in the nanotube plastic deformation under tension. The Stone-Wales transformation, shown in Fig. 3, occurs when an armchair nanotube is stressed in the axial direction. Nardelli et al. [12] theorized that the Stone-Wales transformation results in ductile fracture for armchair nanotubes.

## 2.2. Nanotube morphology

As mentioned before, fullerenes are closed, convex cages that are composed of pentagons and hexagons. The Stone-Wales transformation introduces a new defect in the nanotube structure, the heptagon. Heptagons allow for concave areas within the nanotube. Thus, the heptagonal defects in nanotubes can result in many possible equilibrium shapes. Indeed, most nanotubes are not straight cylinders with hemispherical caps.

In addition to different tube morphologies resulting from defects, carbon nanotubes can be single walled or multi-walled structures. Fig. 4 shows a transmission electron microscope (TEM) image showing the nanostructure of a multi-walled carbon nanotube where several layers of graphitic carbon and a hollow core are evident. Multi-walled carbon nanotubes are essentially concentric single walled tubes, where each individual tube can have different chirality. These concentric nanotubes

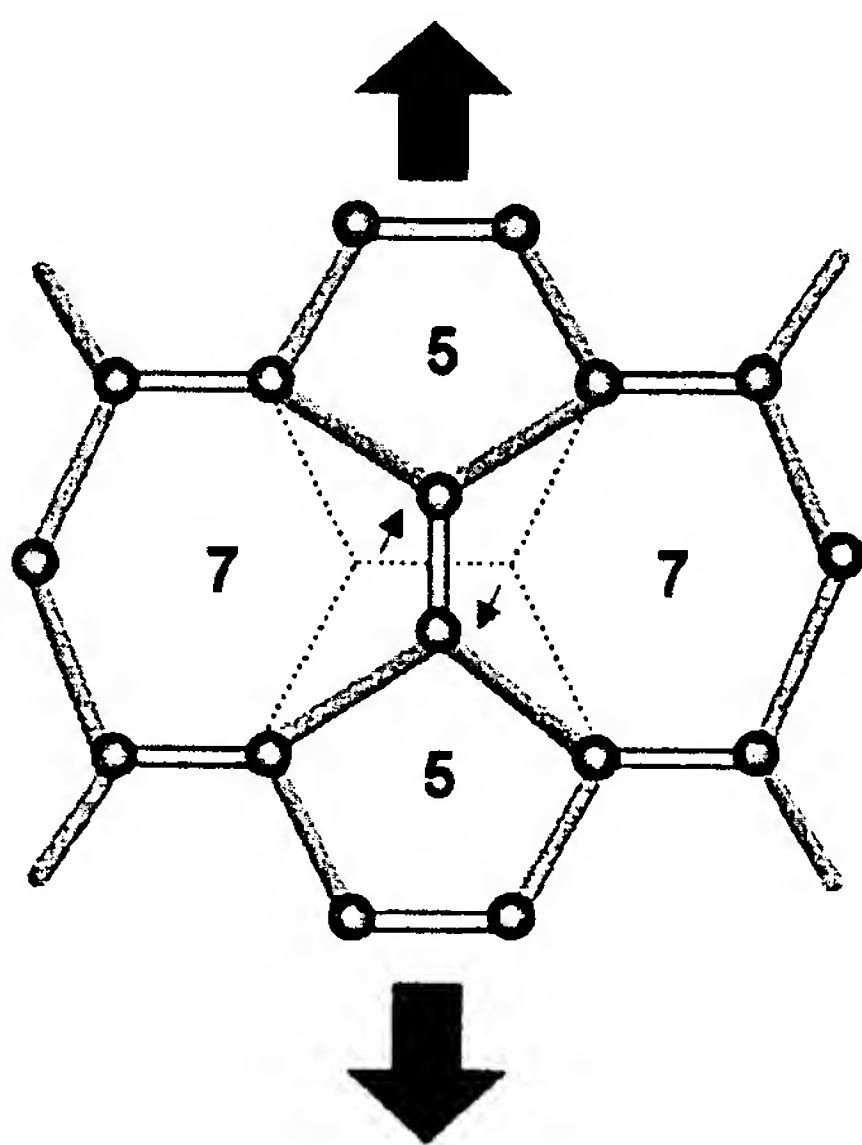


Fig. 3. The Stone-Wales transformation occurring in an armchair nanotube under axial tension.

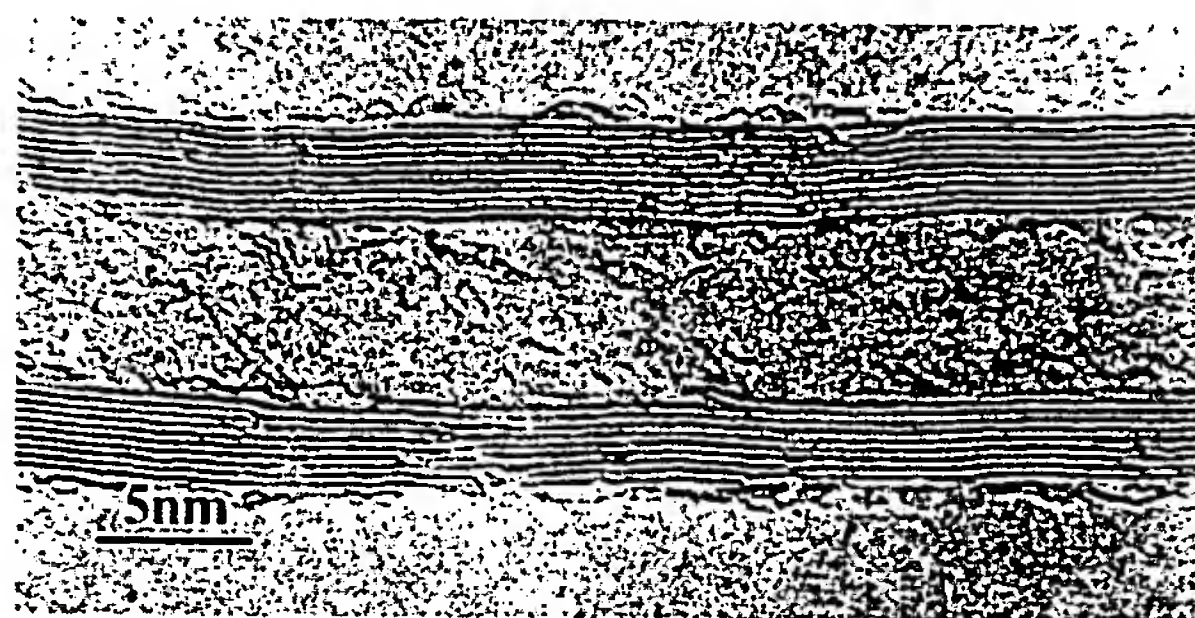


Fig. 4. TEM micrograph showing the layered structure of a multi-walled carbon nanotube.

are held together by secondary, van der Waals bonding. Single-walled nanotubes are most desired for fundamental investigations of the structure/property relationships in carbon nanotubes, since the intra-tube interactions further complicate the properties of carbon nanotubes. Indeed, both single and multi-walled nanotubes show unique properties that can be exploited for use in composite materials.

## 3. Processing of carbon nanotubes for composite materials

Since carbon nanotubes were discovered nearly a decade ago, there have been a variety of techniques developed for producing them. Iijima [1] first observed multi-walled nanotubes, and Iijima et al. [13] and Bethune et al. [14] independently reported the synthesis of single-walled nanotubes a few years later. Primary synthesis methods for single and multi-walled carbon nanotubes include arc-discharge [1,15], laser ablation [16], gas-phase catalytic growth from carbon monoxide [17], and chemical vapor deposition (CVD) from hydrocarbons [18–20] methods. For application of carbon nanotubes in composites, large quantities of nanotubes are required, and the scale-up limitations of the arc discharge and laser ablation techniques would make the cost of nanotube-based composites prohibitive. During nanotube synthesis, impurities in the form of catalyst particles, amorphous carbon, and non-tubular fullerenes are also produced. Thus, subsequent purification steps are required to separate the tubes. The gas-phase processes tend to produce nanotubes with fewer impurities and are more amenable to large-scale processing. It is the authors' belief that gas-phase techniques, such as CVD, for nanotube growth offer the greatest potential for the scaling-up of nanotube production for the processing of composites. In this section, we briefly review the primary techniques for producing carbon nanotubes and some of the benefits and drawbacks of each technique.

Iijima [1] first observed nanotubes synthesized from the electric-arc discharge technique. Shown schematically in Fig. 5, the arc discharge technique generally

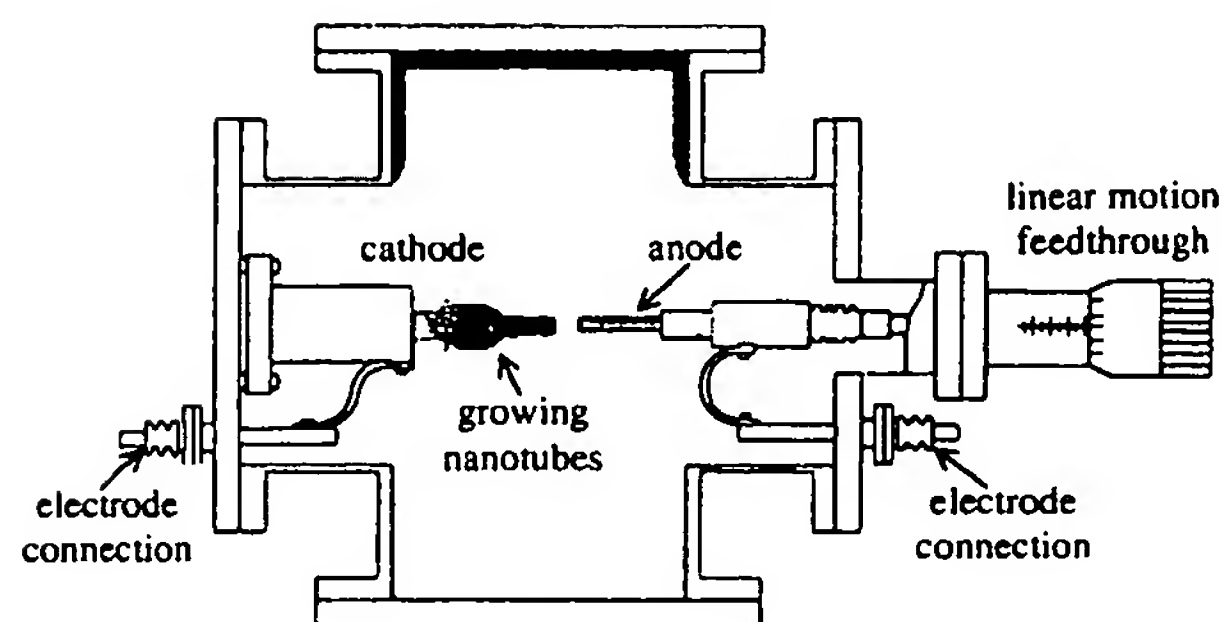


Fig. 5. Schematic illustration of the arc-discharge technique (after Ref. [22]).

involves the use of two high-purity graphite rods as the anode and cathode. The rods are brought together under a helium atmosphere and a voltage is applied until a stable arc is achieved. The exact process variables depend on the size of the graphite rods. As the anode is consumed, a constant gap between the anode and cathode is maintained by adjusting the position of the anode. The material then deposits on the cathode to form a build-up consisting of an outside shell of fused material and a softer fibrous core containing nanotubes and other carbon particles. To achieve single walled nanotubes, the electrodes are doped with a small amount of metallic catalyst particles [13–15,21,22].

Laser ablation was first used for the initial synthesis of fullerenes. Over the years, the technique has been improved to allow the production of single-walled nanotubes [16,23,24]. In this technique, a laser is used to vaporize a graphite target held in a controlled atmosphere oven at temperatures near 1200 °C. The general set-up for laser ablation is shown in Fig. 6. To produce single-walled nanotubes, the graphite target was doped with cobalt and nickel catalyst [16]. The condensed material is then collected on a water-cooled target.

Both the arc-discharge and the laser-ablation techniques are limited in the volume of sample they can produce in relation to the size of the carbon source (the anode in arc-discharge and the target in laser ablation). In addition, subsequent purification steps are necessary to separate the tubes from undesirable by-products. These limitations have motivated the development of gas-phase techniques, such as chemical vapor deposition (CVD), where nanotubes are formed by the decomposition of a carbon-containing gas. The gas-phase techniques are amenable to continuous processes since the carbon source is continually replaced by flowing gas. In addition, the final purity of the as-produced nanotubes can be quite high, minimizing subsequent purification steps.

Nikolaev et al. [17] describe the gas-phase growth of single-walled carbon nanotubes with carbon monoxide as the carbon source. They reported the highest yields of single walled nanotubes occurred at the highest accessible temperature and pressure (1200 °C, 10 atm).

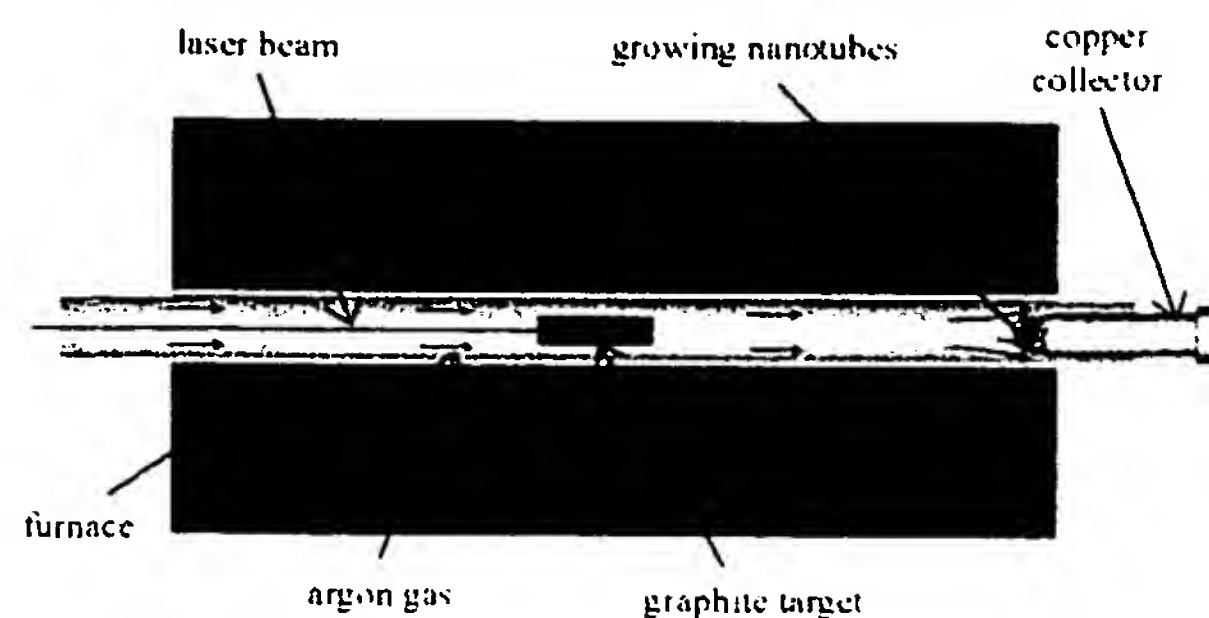


Fig. 6. Schematic of the laser ablation process (after Ref. [4]).

Smalley and his co-workers at Rice University have refined the process to produce large quantities of single-walled carbon nanotubes with remarkable purity. The so-called HiPco nanotubes (high-pressure conversion of carbon monoxide) have received considerable attention as the technology has been commercialized by Carbon Nanotechnologies Inc (Houston, TX) for large-scale production of high-purity single-walled carbon nanotubes.

Other gas-phase techniques utilize hydrocarbon gases as the carbon source for production of both single and multi-walled carbon nanotubes via CVD [25–28]. Nikolaev and co-workers [17] point out that hydrocarbons pyrolyze readily on surfaces heated above 600–700 °C. As a consequence, nanotubes grown from hydrocarbons can have substantial amorphous carbon deposits on the surface of the tubes and will require further purification steps. Although the disassociation of hydrocarbons at low temperatures affects the purity of the as-processed nanotubes, the lower processing temperature enables the growth of carbon nanotubes on a wide variety of substrates, including glass.

One unique aspect of CVD techniques is its ability to synthesize aligned arrays of carbon nanotubes with controlled diameter and length. The synthesis of well-aligned, straight carbon nanotubes on a variety of substrates has been accomplished by the use of plasma-enhanced chemical vapor deposition (PECVD) where the plasma is excited by a DC source [18–20] or a microwave source [29–33]. Fig. 7a and b shows the ability to grow straight carbon nanotubes over a large area with excellent uniformity in diameter, length, straightness, and site density. Adjusting the thickness of the catalyst layer controls the diameter of the tubes, shown in Fig. 8a and b.

In CVD growth of straight carbon nanotube arrays, described by Ren et al. [19] a substrate is first coated with a layer of nickel catalyst. High-purity ammonia is then used as the catalytic gas and acetylene as the carbon source. A direct-current power generates the required plasma, and a deeply carbonized tungsten filament assists the dissociation of the reactive gases and supplies heat to the substrate. Control over the nanotube length



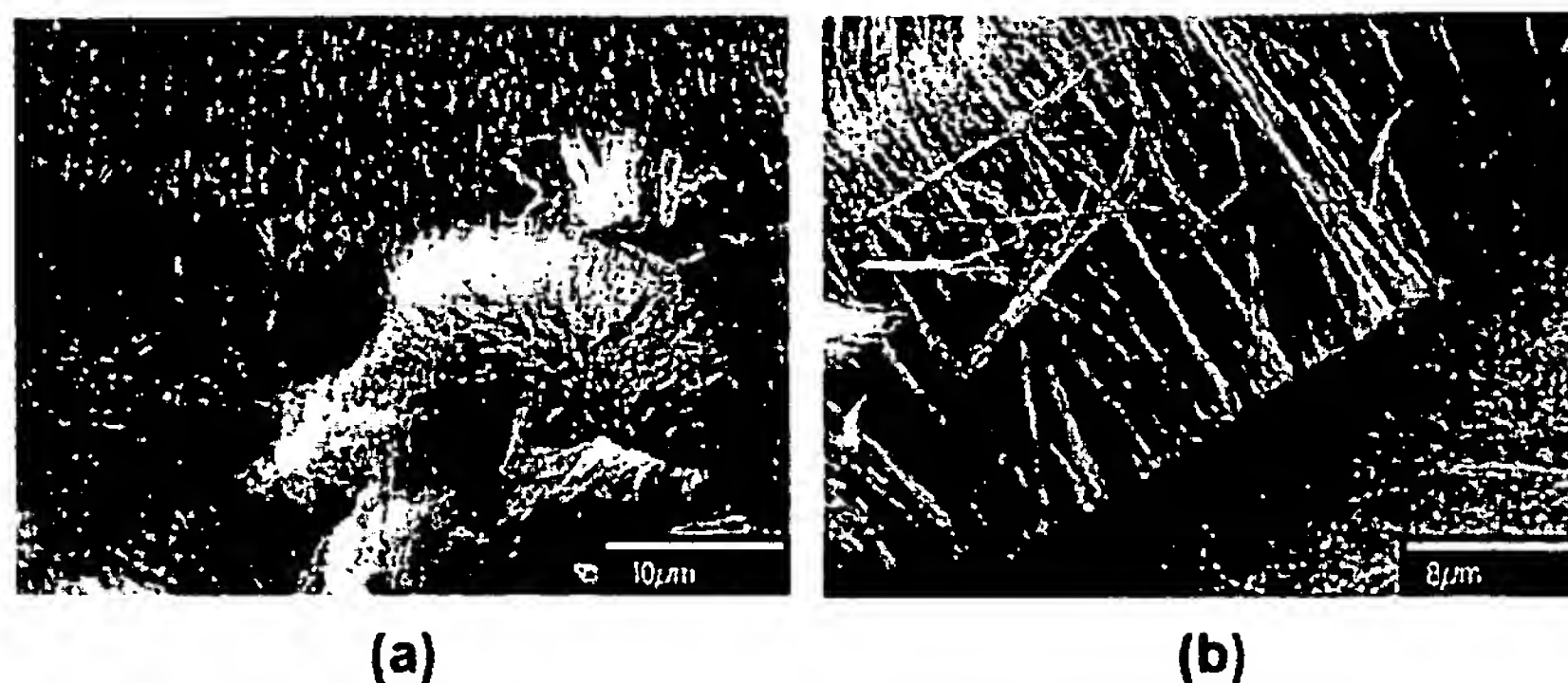


Fig. 7. Micrographs showing the straightness of MWCNTs grown via PECVD [19].

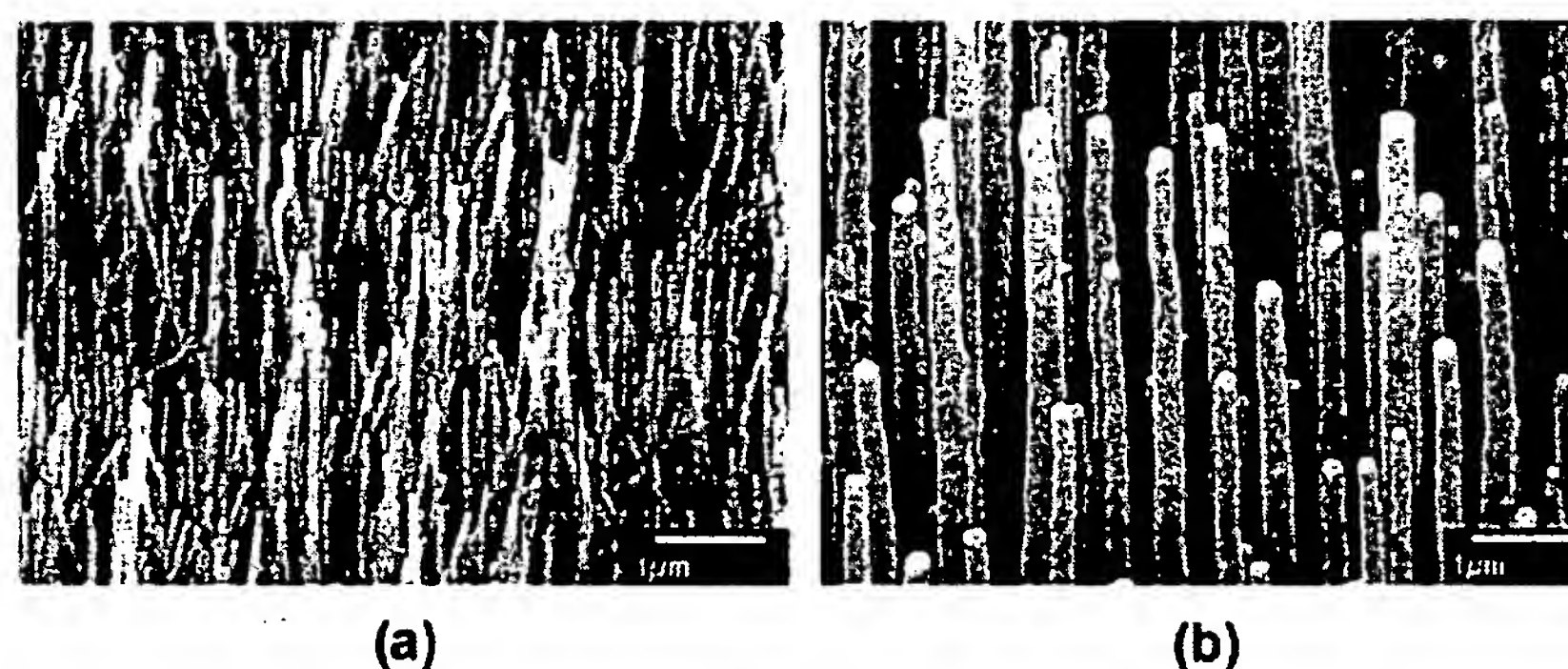


Fig. 8. Micrographs showing control over the nanotube diameter: (a) 40–50 nm and (b) 200–300 nm aligned carbon nanotubes [19].

and graphitization is accomplished by changing the growth time and temperature, respectively, and application of the DC plasma results in tube growth in the direction of the plasma. The use of an alternating microwave frequency source to excite the plasma results in the growth of carbon nanotubes that occur directly normal to the surface of the substrate. Bower et al. [29] showed that in microwave plasma-enhanced CVD (MPECVD) alignment of the carbon nanotubes results from the self-bias that is imposed on the surface of the substrate from the microwave plasma. Fig. 9a shows the alignment of carbon nanotubes grown normal to the surface of an optical glass fiber. To gain further insight into the mechanism for tube alignment, the tubes were grown for two minutes under the microwave-induced plasma followed by 70 min with the plasma off. Fig. 9b shows the results of this experiment. The upper portion of the nanotubes are straight, indicating alignment in the plasma, and the base shows a random, curled structure associated with thermal CVD. In addition, the growth rate under the plasma enhancement was 40 times faster than the thermal CVD.

In addition to highly aligned arrays of carbon nanotubes, large quantities of carbon nanotubes can be processed by conventional CVD techniques. Unlike PECVD, which requires the use of specialized plasma equipment, tangled carbon nanotubes are grown in a

tube furnace. Fig. 10 is a SEM micrograph of the furnace-grown carbon nanotubes showing the same random, curled structure associated with thermal CVD (shown in Fig. 9). The outer diameters of these tubes range from 10–50 nm. These tangled, spaghetti-like nanotubes can be produced at a larger quantity and lower cost than PECVD tubes, but there is less control over length, diameter, and structure.

#### 4. Characterization of carbon nanotubes

Significant challenges exist in both the micromechanical characterization of nanotubes and the modeling of the elastic and fracture behavior at the nano-scale. Challenges in characterization of nanotubes and their composites include (a) complete lack of micromechanical characterization techniques for direct property measurement, (b) tremendous limitations on specimen size, (c) uncertainty in data obtained from indirect measurements, and (d) inadequacy in test specimen preparation techniques and lack of control in nanotube alignment and distribution.

In order better to understand the mechanical properties of carbon nanotubes, a number of investigators have attempted to characterize carbon nanotubes directly. Treacy et al. [34] first investigated the elastic modulus of isolated multi-walled nanotubes by measuring, in the



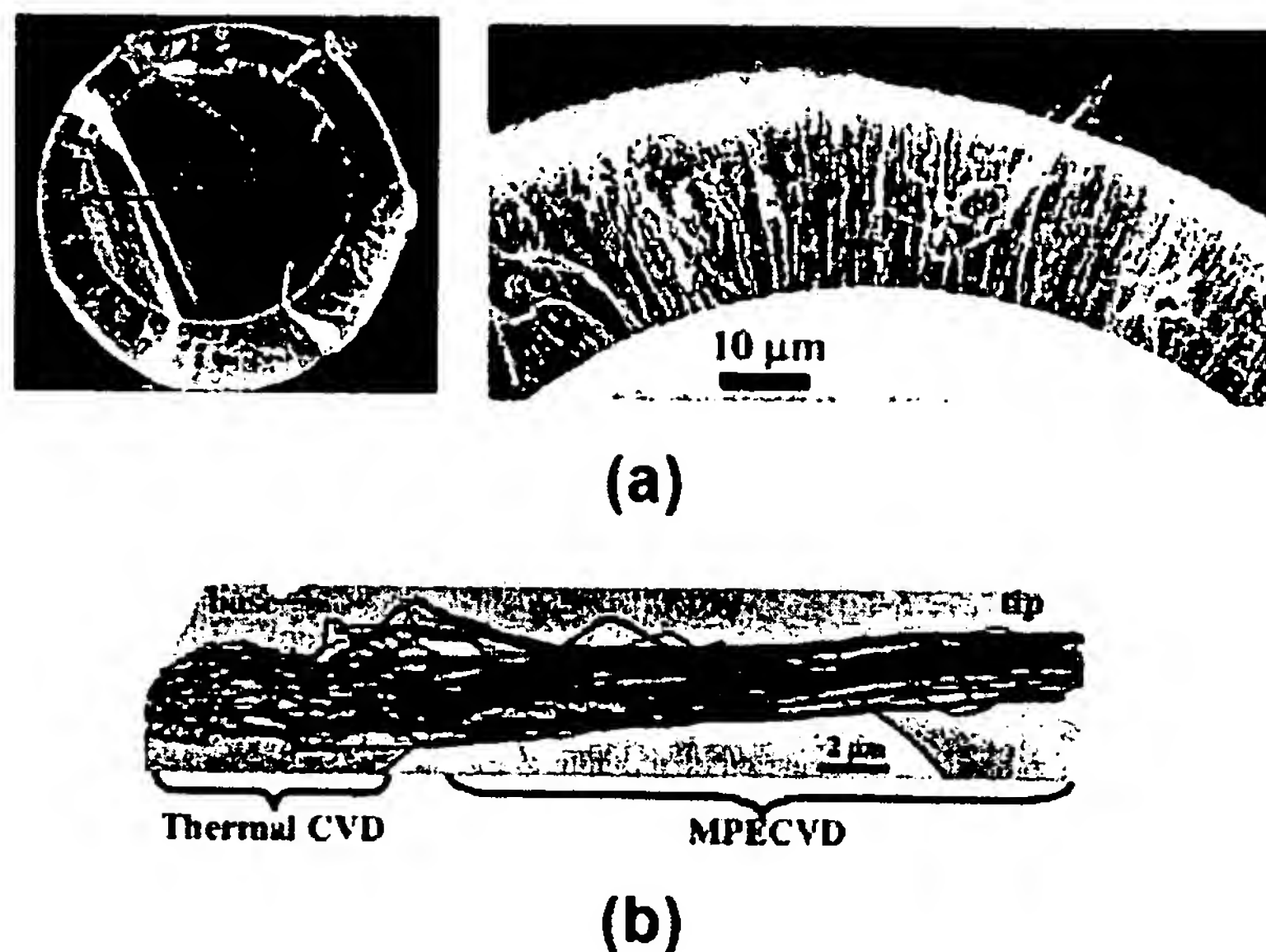


Fig. 9. Micrographs showing (a) nanotubes aligned normal to the surface of a glass fiber and (b) the influence of MPECVD on the structure of the nanotubes [29].

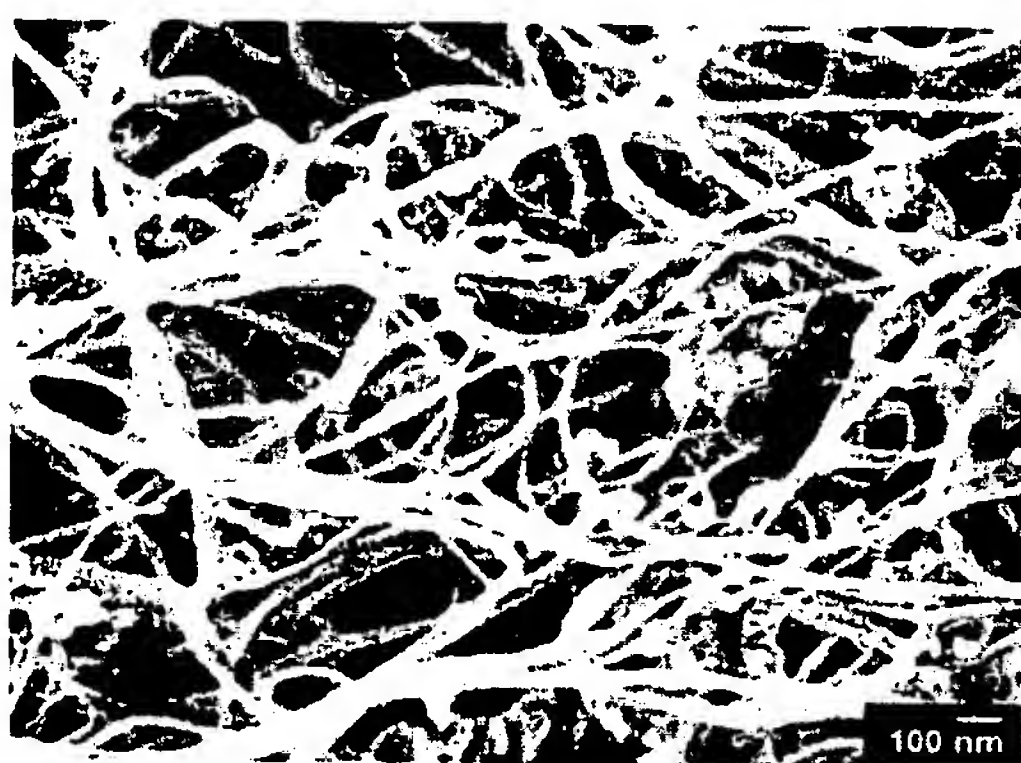


Fig. 10. Micrograph showing tangled, spaghetti-like carbon nanotubes grown with conventional CVD techniques.

transmission electron microscope, the amplitude of their intrinsic thermal vibration. The average value obtained over 11 samples was 1.8 TPa. Direct measurement of the stiffness and strength of individual, structurally isolated multi-wall carbon nanotubes has been made with an atomic-force microscope (AFM). Wong and co-workers [35] were the first to perform direct measurement of the stiffness and strength of individual, structurally isolated multi-wall carbon nanotubes using atomic force microscopy. The nanotube was pinned at one end to molybdenum disulfide surfaces and load was applied to the tube by means of the AFM tip. The bending force was measured as a function of displacement along the unpinned length, and a value of 1.26 TPa was obtained for the elastic modulus. The average bending strength measured was  $14.2 \pm 8$  GPa.

Single-walled nanotubes tend to assemble in 'ropes' of nanotubes. Salvétat and co-workers [35] measured the properties of these nanotube bundles with the AFM. As the diameter of the tube bundles increases, the axial and shear moduli decrease significantly. This suggests slipping of the nanotubes within the bundle. Walters et al. [37] further investigated the elastic strain of nanotube bundles with the AFM. On the basis of their experimental strain measurements and an assumed elastic modulus of 1.25 TPa, they calculated a yield strength of  $45 \pm 7$  GPa for the nanotube ropes. Indeed, their calculated value for strength would be much lower if the elastic modulus of the nanotube bundle is decreased as a consequence of slipping within the bundle, suggested by Salvétat et al. [36].

Yu and co-workers [38,39] have investigated the tensile loading of multi-walled nanotubes and single-walled nanotube ropes. In their work, the nanotubes were attached between two opposing AFM tips and loaded under tension. Their experimental set-up is shown in Fig. 11. For multi-walled carbon nanotubes [38] the failure of the outermost tube occurred followed by pull-out of the inner nanotubes. This 'sword and sheath' telescoping failure mechanism of multi-walled carbon nanotubes in tension is also shown in Fig. 11. The experimentally calculated tensile strengths of the outermost layer ranged from 11 to 63 GPa and the elastic modulus ranged from 270 to 950 GPa. In their subsequent investigation of single-walled nanotube ropes [39], they assumed that only the outermost tubes assembled in the rope carried the load during the experiment, and they calculated tensile strengths of 13 to 52 GPa and average elastic moduli of 320 to 1470 GPa. Xie et

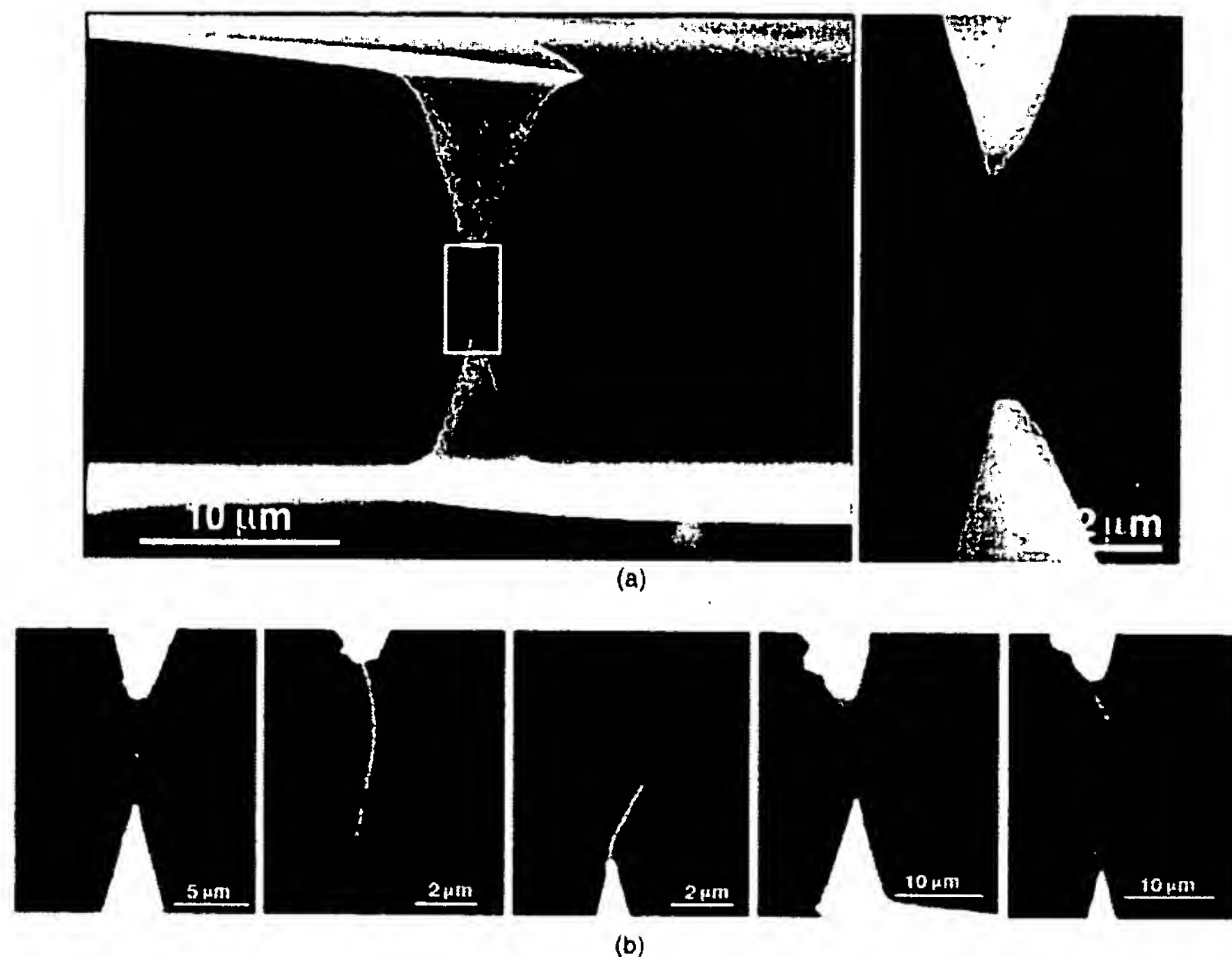


Fig. 11. Micrographs showing (a) the apparatus for tensile loading of MWCNTs and (b) the telescoping, "sword and sheath" fracture behavior of the MWCNT [38].

al. [40] also tested ropes of multi-walled nanotubes in tension. In their experiments, the obtained tensile strength and modulus were 3.6 and 450 GPa, respectively. It was suggested that the lower values for strength and stiffness may be a consequence of defects in the CVD-grown nanotubes.

## 5. Mechanics of carbon nanotubes

As discussed in the previous section, nanotube deformation has been examined experimentally. Recent investigations have shown that carbon nanotubes possess remarkable mechanical properties, such as exceptionally high elastic modulus [34,35], large elastic strain and fracture strain sustaining capability [41,42]. Similar conclusions have also been reached through some theoretical studies [43–46], although very few correlations between theoretical predictions and experimental studies have been made. In this section we examine the mechanics of both single walled and multi-walled nanotubes.

### 5.1. Single-walled carbon nanotubes

Theoretical studies concerning the mechanical properties of single-walled nanotubes have been pursued extensively. Overney et al. [43] studied the low-frequency vibrational modes and structural rigidity of long nanotubes consisting of 100, 200 and 400 atoms. The calculations were based on an empirical Keating Hamiltonian

with parameters determined from first principles. A comparison of the bending stiffnesses of single-walled nanotubes and an iridium beam was presented. The bending stiffness of the iridium beam was deduced by using the continuum Bernoulli-Euler theory of beam bending. Overney and co-workers concluded that the beam bending rigidity of a nanotube exceeds the highest values found in any other presently available materials.

Besides their experimental observations, Iijima et al. [47] examined response of nanotubes under compression using molecular dynamics simulations. They simulated the deformation properties of single- and multi-walled nanotubes bent to large angles. Their experimental and theoretical results show that nanotubes are remarkably flexible. The bending is completely reversible up to angles in excess of  $110^\circ$ , despite the formation of complex kink shapes. Fig. 12 shows their numerical and experimental results, demonstrating the exceptional resilience of carbon nanotubes at large strain.

Ru [48] noticed that actual bending stiffness of single-walled nanotubes is much lower than that given by the elastic-continuum shell model if the commonly defined representative thickness is used. Ru proposed the use of an effective nanotube bending stiffness as a material parameter not related to the representative thickness. With the aid of this concept, the elastic shell equations can be readily modified and then applied to single-walled nanotubes. The computational results based on this concept show a good agreement with the results from molecular dynamics simulations.

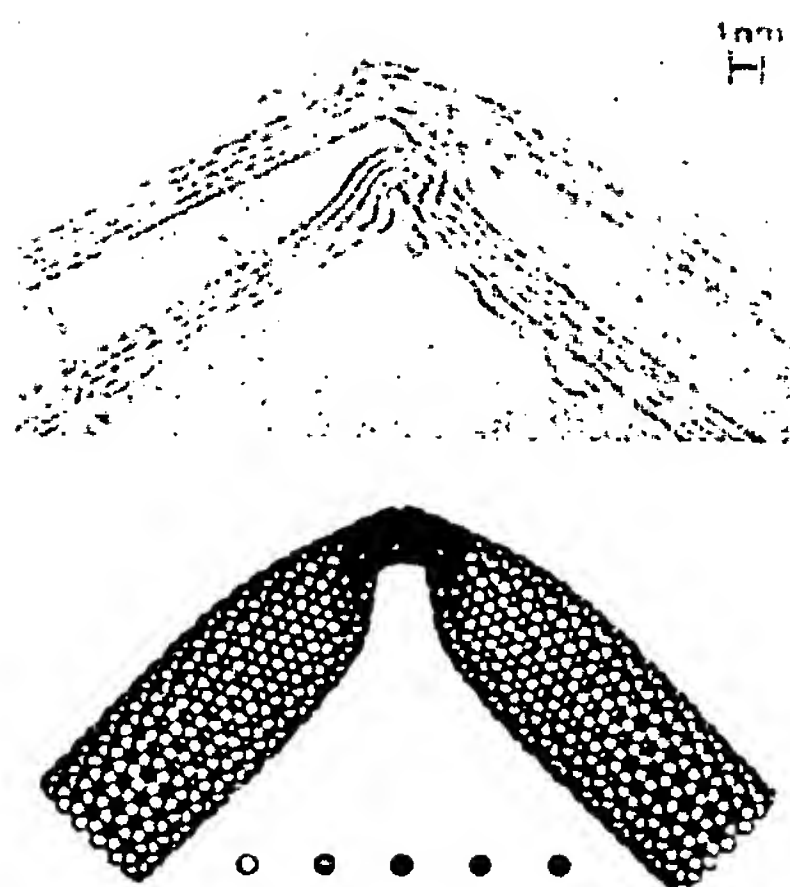


Fig. 12. TEM micrograph and computer simulation of nanotube buckling [47].

Vaccarini et al. [49] investigated the influence of nanotube structure and chirality on the elastic properties in tension, bending, and torsion. They found that the chirality played a small influence on the nanotube tensile modulus. However, the chiral tubes exhibit asymmetric torsional behavior with respect to left and right twist, whereas the armchair and zigzag tubes do not exhibit this asymmetric torsional behavior.

A relatively comprehensive study of the elastic properties of single-walled nanotubes was reported by Lu [44]. In this study, Lu adopted an empirical lattice-dynamics model [50], which has been successfully adopted in calculating the phonon spectrum and elastic properties of graphite. In this lattice-dynamics model, atomic interactions in a single carbon layer are approximated by a sum of pair-wise harmonic potentials between atoms. The local structure of a nanotube layer is constructed from conformal mapping of a graphite sheet on to a cylindrical surface. Lu's work attempted to answer such basic questions as: (a) how do elastic properties of nanotubes depend on the structural details, such as size and chirality? and (b) how do elastic properties of nanotubes compare with those of graphite and diamond? Lu concluded that the elastic properties of nanotubes are insensitive to size and chirality. The predicted Young's modulus ( $\sim 1$  TPa), shear modulus ( $\sim 0.45$  TPa), and bulk modulus ( $\sim 0.74$  TPa) are comparable to those of diamond. Hernandez and co-workers [51] performed calculations similar to those of Lu and found slightly higher values ( $\sim 1.24$  TPa) for the Young's moduli of tubes. But unlike Lu, they found that elastic moduli are sensitive to both tube diameter and structure.

Besides their unique elastic properties, the inelastic behavior of nanotubes has also received considerable attention. Yakobson and co-workers [10,46] examined the instability behavior of carbon nanotubes beyond linear response by using a realistic many-body Tersoff-Brenner

potential and molecular dynamics simulations. Their molecular-dynamics simulations show that carbon nanotubes, when subjected to large deformations, reversibly switch into different morphological patterns. Each shape change corresponds to an abrupt release of energy and a singularity in the stress/strain curve. These transformations are explained well by a continuum shell model. With properly chosen parameters, their model provided a very accurate 'roadmap' of nanotube behavior beyond the linear elastic regime. They also made molecular dynamics simulations to single- and double-walled nanotubes of different chirality and at different temperatures [45]. Their simulations show that nanotubes have an extremely large breaking strain (in the range 30–40%) and the breaking strain decreases with temperature. Yakobson [11] also applied dislocation theory to carbon nanotubes for describing their main routes of mechanical relaxation under tension. It was concluded that the yield strength of a nanotube depends on its symmetry and it was believed that there exists an intra-molecular plastic flow. Under high stress, this plastic flow corresponds to a motion of dislocations along helical paths within the nanotube wall and causes a stepwise necking, a well-defined new symmetry, as the domains of different chiral symmetry are formed. As a result, both the mechanical and electronic properties of carbon nanotubes are changed.

The single walled nanotubes produced by laser ablation and arc-discharge techniques have a greater tendency to form 'ropes' or aligned bundles [15,23]. Thus, theoretical studies have been made to investigate the mechanical properties of these nanotube bundles. Ru [52] presented a modified elastic-honeycomb model to study elastic buckling of nanotube ropes under high pressure. Ru gave a simple formula for the critical pressure as a function of nanotube Young's modulus and wall thickness-to-radius ratio. It was concluded that single-walled ropes are susceptible to elastic buckling under high pressure and elastic buckling is responsible for the pressure-induced abnormalities of vibration modes and electrical resistivity of single walled nanotubes.

Popov et al. [53] studied the elastic properties of triangular crystal lattices formed by single-walled nanotubes by using analytical expressions based on a force-constant lattice dynamics model [54]. They calculated various elastic constants of nanotube crystals for nanotube types, such as armchair and zigzag. It was shown that the elastic modulus, Poisson's ratio and bulk modulus clearly exhibit strong dependence on the tube radius. The bulk modulus was found to have a maximum value of 38 GPa for crystals composed of single-walled nanotubes with  $\sim 0.6$  nm radius.

## 5.2. Multi-walled carbon nanotubes

Multi-walled nanotubes are composed of a number of concentric single walled nanotubes held together with



relatively weak van der Waals forces. The multi-layered structure of these nanotubes further complicates the modeling of their properties.

Ruoff and Lorents [55] derived the tensile and bending stiffness constants of ideal multi-walled nanotubes in terms of the known elastic properties of graphite. It is suggested that unlike the strongly anisotropic thermal expansion in conventional carbon fibers and graphite, the thermal expansion of carbon nanotubes is essentially isotropic. However, the thermal conductivity of nanotubes is believed to be highly anisotropic and its magnitude along the axial direction is perhaps higher than that of any other material.

Lu [44] also calculated the elastic properties of many multi-walled nanotubes formed by single-layer tubes by means of the empirical-lattice dynamics model. It was found that elastic properties are insensitive to different combinations of parameters, such as chirality, tube radius and numbers of layers, and the elastic properties are the same for all nanotubes with a radius larger than one nm. Interlayer van der Waals interaction has a negligible contribution to both the tensile and shear stiffness.

Govindjee and Sackman [56] were the first to examine the use of continuum mechanics to estimate the properties of multi-walled nanotubes. They investigated the validity of the continuum approach by using Bernoulli-Euler bending to infer the Young's modulus. They used a simple elastic sheet model and showed that at the nanotube scale the assumptions of continuum mechanics must be carefully respected in order to obtain reasonable results. They showed the explicit dependence of 'material properties' on system size when a continuum cross-section assumption was used.

Ru [57] used the elastic-shell model to study the effect of van der Waals forces on the axial buckling of a double-walled carbon nanotube. The analysis showed that the van der Waals forces do not increase the critical axial buckling strain of a double-walled nanotube. Ru [58,59] thereafter also proposed a multiple column model that considers the interlayer radial displacements coupled through the van der Waals forces. This model was used to study the effect of interlayer displacements on column buckling. It was concluded that the effect of interlayer displacements could not be neglected unless the van der Waals forces are extremely strong.

Kolmogorov and Crespi [60] investigated the interlayer interaction in two-walled nanotubes. A registry-dependent two-body graphite potential was developed. It was demonstrated that the tightly constrained geometry of a multi-walled nanotube could produce an extremely smooth solid-solid interface wherein the corrugation against sliding does not grow with system size. The energetic barrier to interlayer sliding in defect-free nanotubes containing thousands of atoms can be comparable to that for a single unit cell of crystalline graphite.

## 6. Nanotube-based composites

Although there is experimental variability in the direct characterization of carbon nanotubes, theoretical and experimental observations reveal their exceptional properties. As a consequence, there has been recent interest in the development of nanotube-based composites. Although most research has focused on the development of nanotube-based polymer composites, attempts have also been made to develop metal and ceramic-matrix composites with nanotubes as reinforcement. Here we review the recent work in this area and discuss the challenges that are associated with the development of these new composites.

### 6.1. Processing and characterization of nanotube-based polymer composites

The reported exceptional properties of nanotubes have motivated others to investigate experimentally the mechanics of nanotube-based composite films. Uniform dispersion within the polymer matrix and improved nanotube/matrix wetting and adhesion are critical issues in the processing of these nanocomposites.

The issue of nanotube dispersion is critical to efficient reinforcement. In the work of Salvétat et al. [36] discussed earlier, slipping of nanotubes when they are assembled in ropes significantly affects the elastic properties. In addition to slipping of tubes that are not bonded to the matrix in a composite, the aggregates of nanotube ropes effectively reduce the aspect ratio (length/diameter) of the reinforcement. It is, however, difficult to obtain a uniform dispersion of carbon nanotubes in the polymer matrix. Shaffer and Windle [61] were able to process carbon nanotube/polyvinyl-alcohol composite films for mechanical characterization. The tensile elastic modulus and damping properties of the composite films were assessed in a dynamic mechanical thermal analyzer (DMTA) as a function of nanotube loading and temperature. From the theory developed for short-fiber composites, a nanotube elastic modulus of 150 MPa was obtained from the experimental data. This value in a microscopic composite is well below the values reported for isolated nanotubes. It is not clear whether this result is a consequence of imperfections in the graphite layers of catalytically grown nanotubes used for the investigation or whether it relates to a fundamental difficulty in stress transfer.

Qian et al. [62] characterized carbon-nanotube/poly-styrene composites. With only the addition of 1% by weight (about 0.5% by volume) they achieved between 36–42% increase in the elastic stiffness and a 25% increase in the tensile strength. Fig. 13 is a TEM micrograph of their nanotube film showing the mechanisms of fracture. As for conventional fiber composites, we see nanotube pull-out, nanotube fracture, as well as crack

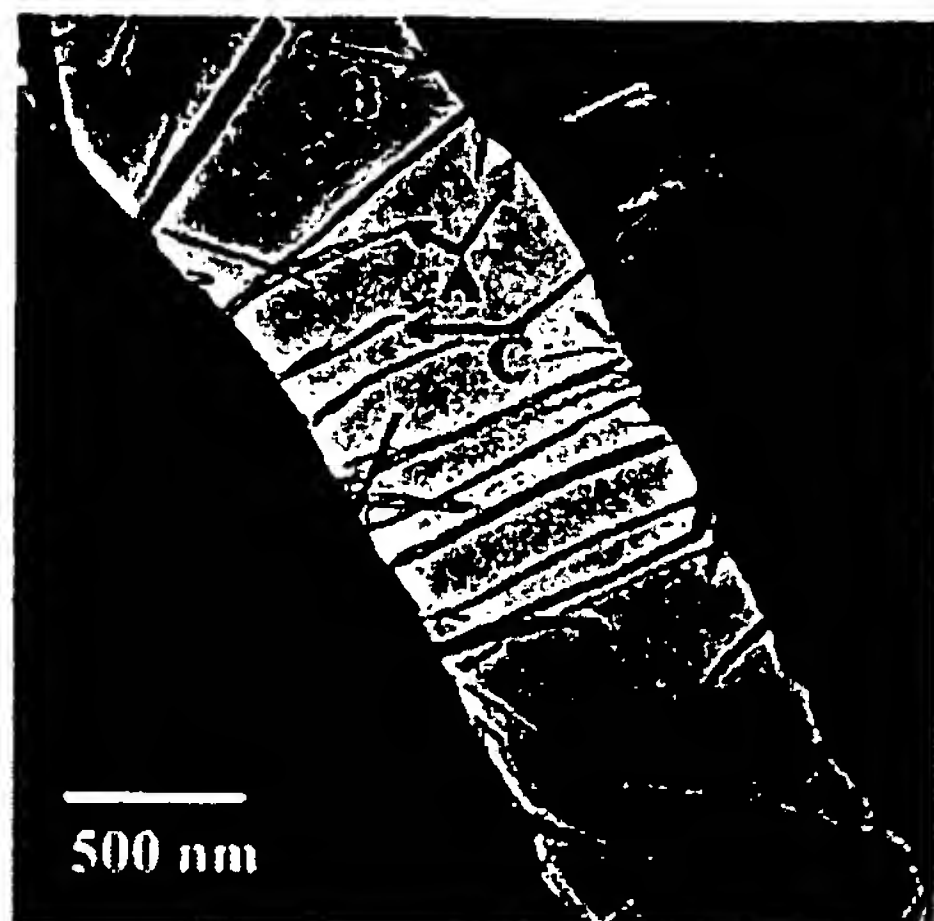


Fig. 13. Fracture mechanisms in nanotube-based composites [62].

bridging by the nanotubes. They also used short-fiber composite theory to demonstrate that 10% by weight of carbon fibers (about 5% by volume) in the research of Tibbetts and McHugh [63] would be required to achieve the same increase in elastic modulus with 1% (by weight) of carbon nanotubes.

Fig. 13 shows significant pull-out of the nanotubes from the matrix. Clearly there is reinforcement as evidenced by improvements in stiffness and strength of the composite, but to take full advantage of the exceptional stiffness, strength, and resilience of carbon nanotubes, strong interfacial bonding is critical. Jia et al. [64] showed that the nanotubes can be initiated by a free-radical initiator, AIBN (2,2'-azobisisobutyronitrile), to open their  $\pi$  bonds. In their study of carbon-nanotube/poly(methyl methacrylate) (PMMA) composites, the possibility exists to form a C–C bond between the nanotube and the matrix. Gong et al. [65] investigated surfactant-assisted processing of nanotube composites with a nonionic surfactant. Improved dispersion and interfacial bonding of the nanotubes in an epoxy matrix resulted in a 30% increase in elastic modulus with addition of 1 wt.% nanotubes.

Lordi and Yao [66] looked at the molecular mechanics of binding in nanotube-based composites. In their work, they used force-field-based molecular-mechanics calculations to determine the binding energies and sliding frictional stresses between pristine carbon nanotubes and different polymeric matrix materials. The binding energies and frictional forces were found to play only a minor role in determining the strength of the interface. The key factor in forming a strong bond at the interface is having a helical conformation of the polymer around the nanotube. They suggested that the strength of the interface may result from molecular-level entanglement of the two phases and forced long-range ordering of the polymer.

Because the interaction at the nanotube/matrix interface is critical to understanding the mechanical behavior of nanotube-based composites, a number of researchers have investigated the efficiency of interfacial stress transfer. Wagner et al. [67] examined stress-induced fragmentation of multi-walled carbon nanotubes in polymer films. Their nanotube-containing film had a thickness of approximately 200  $\mu\text{m}$ . The observed fragmentation phenomenon was attributed to either process-induced stress resulting from curing of the polymer or tensile stress generated by polymer deformation and transmitted to the nanotube. From estimated values of nanotube axial normal stress and elastic modulus, Wagner and co-workers concluded that the nanotube/polymer interfacial shear stress is on the order of 500 MPa and higher. This value, if reliable, is an order of magnitude higher than the stress-transfer ability of current advanced composites and, therefore, such interfaces are more able than either the matrix or the nanotubes themselves to sustain shear. In further work, Lourie and Wagner [68–70] investigated tensile and compressive fracture in nanotube-based composites.

Stress transfer has also been investigated by Raman spectroscopy. Cooper and co-workers [71] prepared composite specimens by applying an epoxy-resin/nanotube mixture to the surface of an epoxy beam. After the specimens were cured, stress transfer between the polymer and the nanotubes was detected by a shift in the  $G'$  Raman band ( $2610\text{ cm}^{-1}$ ) to a lower wavenumber. The shift in the  $G'$  Raman band corresponds to strain in the graphite structure, and the shift indicates that there is stress transfer, and hence reinforcement, by the nanotubes. It was also concluded that the effective modulus of single-walled nanotubes dispersed in a composite could be over 1 TPa and that of multi-walled nanotubes was about 0.3 TPa. In their investigation of single-walled nanotube/epoxy composites, Ajayan et al. [72] suggest that their nearly constant value of the Raman peak in tension is related to tube sliding within the nanotube bundles and, hence, poor interfacial load transfer between the nanotubes. Similar results were obtained by Schadler et al. [73]. Multi-walled nanotube/epoxy composites were tested in both tension and compression. The compressive modulus was found to be higher than the tensile modulus of the composites, and the Raman peak was found to shift only in compression, indicating poor interfacial load transfer in tension.

Even with improved dispersion and adhesion, micro-mechanical characterization of these composites is difficult because the distribution of the nanotubes is random. Thus, attempts have been made to align nanotubes in order better to elucidate the reinforcement mechanisms. Jin et al. [74] showed that aligned nanotube composites could be obtained by mechanical stretching of the composite. X-ray diffraction was used to determine the orientation and degree of alignment.



Bower et al. [42] further investigated the deformation of carbon nanotubes in these aligned films. Haggenueller and co-workers [75] showed that melt spinning of single wall nanotubes in fiber form can also be used to create a well-aligned nanotube composite.

In addition to alignment of the carbon nanotubes, researchers have attempted to spin carbon fibers from carbon nanotubes [76–78]. Andrews et al. [77] dispersed 5 wt.% single-walled nanotubes in isotropic petroleum pitch. Compared to isotropic pitch fibers without nanotubes, the tensile strength was improved by  $\sim 90\%$ , the elastic modulus was improved by  $\sim 150\%$  and the electrical conductivity increased by 340%. Because the pitch matrix is isotropic, the elastic modulus is 10–20 times less than that of mesophase pitch fibers used in composite materials. Further developments in this area may potentially create a new form of carbon fiber that has exceptional flexibility as well as stiffness and strength. Fig. 14 shows the exceptional flexibility of the as-spun nanotube composite fiber produced by Vigolo and co-workers [78]. Their technique for spinning nanotube-based fibers involves dispersing the nanotubes in surfactant solutions followed by recondensing the nanotubes in the stream of a polymer solution to form macroscopic fibers and ribbons. Their work indicates that there is preferential orientation of the nanotubes along the axis of the ribbons. Although the elastic modulus of the nanotube fibers (9–15 GPa) is far below the values for individual nanotubes or conventional carbon fibers, the demonstrated resilience of the fibers gives hope for future improvements.

## 6.2. Ceramic- and metal-matrix composites

The focus of much of the research in nanotube-based composites has been on polymer-matrix materials, but

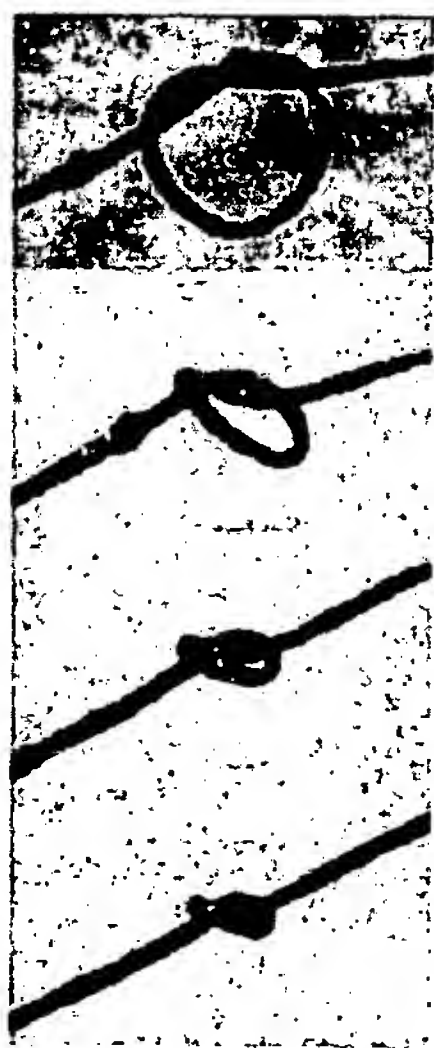


Fig. 14. Micrographs showing the exceptional flexibility of carbon nanotube-based fiber [78].

the unique properties of carbon nanotubes can also be exploited in ceramic- or metal-matrix composites.

Although ceramics have high stiffness and excellent thermal stability with relatively low density, their brittleness impedes the use as structural materials. Because of their exceptional resilience, carbon nanotubes might be particularly desirable as a reinforcement for ceramics. The combination of these nanotubes with a ceramic matrix could potentially create composites that have high-temperature stability as well as exceptional toughness and creep resistance.

Ma and co-workers [79] formed carbon-nanotube/silicon-carbide (SiC) composites via mixing nano-particles of SiC with 10 wt.% carbon nanotubes and hot pressing. They reported a 10% improvement in the strength and fracture toughness as compared to the monolithic ceramics. These modest improvements were attributed to nanotube/matrix debonding and crack deflection. Other researchers [80–84] have developed techniques to synthesize carbon nanotubes in situ to form carbon-nanotube/metal-oxide composite powders. These powders were then hot pressed to form macroscopic composites. The incorporation of the long nanotube bundles grown in situ, however, did not provide the expected improvement in mechanical properties.

Preliminary investigations by Chen et al. [85] focused on synthesis of carbon-nanotube/metal-matrix composites by electroless plating, and Xu et al. [86] showed slight improvements on the electrical conductivity of aluminum with increasing nanotube volume fraction.

## 7. Conclusions

The exceptional mechanical and physical properties demonstrated for carbon nanotubes, combined with their low density, make this new form of carbon an excellent candidate for composite reinforcement. Before these extraordinary properties observed at the nano-scale are realized in a macroscopic composite, considerable basic research is necessary. Full understanding of the thermo-mechanical behavior of nanotube-based composites, requires knowledge of the elastic and fracture properties of carbon nanotubes as well as of interactions at the nanotube/matrix interface. Although this requirement is no different from that in conventional fiber composites [3], the scale of the reinforcement phase diameter has changed from micrometer (e.g. glass and carbon fibers) to nano-meter. The change in reinforcement scale poses new challenges in the development of processing techniques for these composites as well as the development of characterization techniques and methodologies to measure the elastic and fracture behavior of carbon nanotubes and their composites. The nano-meter scale of the reinforcement presents additional

challenges in mechanics research since we now must account for interactions at the atomic-scale.

Preliminary research in nanotube-based composites has indicated that there is potential in carbon nanotubes for reinforcement, but, most importantly, it has illustrated the significant challenges that must be overcome before the potential is realized. Critical to the use of nanotubes as a structural material, there is a need for development of nanotube production techniques at the scale needed for producing macroscopic composites that are cost-effective. Fundamental work in processing, characterization, and analysis/modeling is crucial before the structural and functional properties of this new class of nanocomposites can be optimized.

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